

# THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

## ORDINARY MEETING

AN Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, November 7th, 1956, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President, Dr. K. A. Williams, A.Inst.P., M.Inst.Pet., F.R.I.C.

The following paper was presented and discussed: "The Structure of Dithizone and its Metal Complexes," by H. M. N. H. Irving, M.A., D.Phil., F.R.I.C., L.R.A.M.

## NEW MEMBERS

### ORDINARY MEMBERS

Michael Moffatt Crowder, M.Sc.Tech.; Hilda Irene Fisk, B.Sc. (Lond.); John Cyril House; Dong-Suh Ling, B.Sc. (Shanghai); Matthew Lonsdale; David Milton Raistrick, B.Sc. (Manc.), A.R.I.C.; Peter George William Scott, B.Sc. (Lond.), A.R.I.C.; John W. Skirvin, B.S. (Fairfield); Peter Reid Wood.

### JUNIOR MEMBERS

Frank Robert Coe, B.Sc. (Birm.); Albert Thomas Masters, B.Sc. (Lond.); William Frank Turton.

## DEATH

We record with regret the death of

Arthur Eric Jarvis Vickers.

## SCOTTISH SECTION

A JOINT Meeting of the Section with the Methods of Analysis Panel (Glasgow) was held at 7.15 p.m. on Friday, September 28th, 1956, at the Central Station Hotel, Glasgow. The Chair was taken by the Chairman of the Section, Dr. F. J. Elliott, F.R.I.C., F.R.S.E.

The following papers were presented and discussed: "The Photometric Determination of Molybdenum as the Thiocyanate," by R. Kerr, B.Sc., A.R.I.C.; "The Determination of Copper in Steel," by L. J. A. Haywood and P. Sutcliffe; "The Analysis of Titanium and its Alloys," by W. T. Elwell, F.R.I.C.

## WESTERN SECTION

THE South-Western Counties Section of the Royal Institute of Chemistry held a meeting on Saturday, October 6th, 1956, at 2.30 p.m., at the Technical College, Plymouth, in which the Western Section were invited to participate. The Chair was taken by the Chairman of the South-Western Counties Section, Dr. F. D. M. Hocking, M.Sc., M.B., B.S., L.R.C.P., M.R.C.S., A.C.G.F.C., M.I.Biol., F.R.I.C.

The meeting took the form of a Symposium on "Careers in Chemistry" and a general discussion was opened with special contributions from J. W. Barrett, B.Sc., Ph.D., A.R.C.S., D.I.C., A.M.I.Chem.E., F.R.I.C., Professor H. T. S. Britton, D.Sc., D.I.C., F.R.I.C., J. Idris Jones, M.Sc., D.Sc., F.R.I.C., and A. C. Truman, B.Sc., A.R.I.C.

A JOINT Meeting of the Section with the Cardiff and District Section of the Royal Institute of Chemistry and the South Wales Section of the Society of Chemical Industry was held at 7 p.m. on Wednesday, October 10th, 1956, at the Technical College, Newport, Mon. The Chair was taken by the Chairman of the Section, Mr. P. J. C. Haywood, B.Sc., F.R.I.C.

A lecture on "Sequestering Agents and their Analytical Applications" was given by R. L. Smith, B.Sc., Ph.D., A.R.I.C.

#### MIDLANDS SECTION

AN Ordinary Meeting of the Section was held at 7.15 p.m. on Thursday, September 27th, 1956, in the Lecture Theatre, Derby and District College of Art, Green Lane, Derby. The Chair was taken by the Chairman of the Section, Mr. J. R. Leech, J.P.

The following paper was presented and discussed: "High-precision Absorptiometry," by W. T. L. Neal, B.A., A.R.I.C.

AN additional Ordinary Meeting of the Section was held at 7 p.m. on Friday, September 28th, 1956, in the Main Chemistry Theatre, The University, Edgbaston, Birmingham, 15. The Chair was taken by the Chairman of the Section, Mr. J. R. Leech, J.P.

The following paper was presented and discussed: "Precipitation from Homogeneous Solution," by Professor L. Gordon (Syracuse University).

AN Ordinary Meeting of the Section was held at 7 p.m. on Thursday, October 25th, 1956, in the Gas Showrooms, Nottingham. The Chair was taken by the Chairman of the Section, Mr. J. R. Leech, J.P.

The following paper was presented and discussed: "Recent Advances in Ion-exchange Resins," by D. K. Hale, M.A.

## Non-ferrous Metallurgical Analysis

### A Review

By G. W. C. MILNER

IMPORTANT developments have taken place in this branch of analytical chemistry. Many determinations that used to be carried out by classical procedures are now accomplished by more direct physico-chemical methods. The time-consuming gravimetric procedures have been replaced in the most part by these more modern methods. Volumetric methods, however, are still fairly widely applied to the determination of certain major alloying constituents and, more recently, the development of ethylenediaminetetra-acetic acid (EDTA) as a volumetric reagent has extended these methods to the determination of some of the more difficult elements, such as zirconium and thorium.

The physico-chemical methods either eliminate chemical separations completely or else reduce them to a minimum, and by this means a great saving in time and manpower is effected, especially in control laboratories in which many alloys of the same type are analysed. Absorptiometry is one of the more important of the modern techniques, because the necessary equipment is not too expensive, and most elements forming stable coloured complexes can be determined by it. It is especially suitable for the determination of minor alloying constituents and also for trace impurities in pure metals. More recently, however, it has proved useful in certain instances for the determination of major alloying constituents by the application of a differential method of measurement. Conventional polarography is often used for the determination of those minor alloying elements that do not form coloured complexes readily. Lead and zinc are two constituents in non-ferrous analysis for which this technique is most suitable. Polarographic methods are bound to find a much wider application in the future, however, through the development of square-wave polarography.<sup>1</sup> With this instrument minor alloying constituents can be directly determined in the presence of major constituents reducing at the dropping-mercury electrode at more positive potentials than do the minor constituents, and this behaviour permits several elements to be determined from a single recording of the polarogram.

Electrolytic methods in which platinum electrodes are employed have always been most useful for certain determinations in non-ferrous metallurgical analysis. Their application in recent years, however, has been made more selective through the development of equipment for controlling the potential of the cathode at pre-selected values.<sup>2</sup> The author<sup>3</sup> has found this technique very useful in a scheme for the analysis of copper-base alloys. After the separation of the copper from a hydrochloric acid solution of the sample by controlling the potential of the cathode at -0.36 volt against the saturated-calomel electrode (S.C.E.), the amount of this constituent is determined from the increase in weight of the cathode. Then the electrolysis is repeated with the cathode controlled at -0.70 volt against the S.C.E. to obtain the simultaneous deposition of lead and tin. The iron, manganese and nickel contents are determined in the remaining electrolyte by absorptiometric methods, whilst values for the aluminium and zinc contents are obtained by volumetric methods. One controlling unit is required for each pair of electrodes, and this makes the procedure more suitable for the analysis of occasional samples than for routine samples. However, this example does show how modern techniques have been combined to resolve difficult analytical problems. Electrolysis is also of value for the separation of various elements from a major constituent before their amounts are determined by some suitable physico-chemical technique. The main advantage of this method is that the separation is effected without the addition of any chemicals to the sample solution. Also, when the platinum cathode is replaced by a stirred-mercury cathode, the values of the cathode potential needed to effect the required separations can be forecast from polarographic half-wave potential data. The determination of small amounts of zinc in cadmium metal is a good example of the value of this method.<sup>4</sup> The cadmium is deposited into the mercury cathode controlled at  $-1.00 \pm 0.02$  volt against the S.C.E. when an ammoniacal solution of the sample is electrolysed. Then a small amount of gelatin is added to a quantity of the electrolyte and the amount of zinc is determined from the height of the polarographic step occurring in the region of -1.3 volts against the

S.C.E. Lingane used this electrolytic method only when it proved impossible to effect the necessary separation by precipitating the cadmium as hydroxide with sodium hydroxide.

Separations by solvent extraction are a great improvement in many instances on the conventional precipitation methods. Cellulose chromatography is an extended form of solvent extraction, and separations that are most difficult by precipitation methods have been readily effected by this technique, as for example, the separation of niobium and tantalum from each other.<sup>5,6</sup>

Activation analysis has become more important in this country in recent years, because of the availability of the Harwell pile for the irradiation of samples. This method is useful for the determination of those elements that produce radioactive isotopes with suitable half-lives on neutron bombardment in the pile. It is most valuable for the determination of trace constituents in materials, since the method is free from the reagent-blank difficulties that affect most physico-chemical methods. The activation method is not a rapid method of analysis, because after the addition of carrier it is often necessary to separate the required isotope from all the other activity produced by the irradiation of the sample. It does, however, provide another technique for the analyst to use in the solution of problems that are either very difficult or impossible by other methods. Chemical separations after irradiation can be avoided when the constituent being determined produces a  $\gamma$ -emitting isotope, and then determination can often be completed by direct  $\gamma$ -radiation spectrometry. The separations in this type of work are greatly simplified by the use of ion-exchange resins. This is because complete recovery of the added carrier is not necessary; the main requirement is for the recovery of a weighable amount of this constituent, which must, however, be radiochemically pure. The determination of sub-microgram amounts of sodium in lithium metal by activation analysis is an excellent example of a determination that could not be accomplished by any other procedure. Undoubtedly this technique will find wider applications in the future when more facilities for the irradiation of samples become available.

Emission spectroscopy is a more physical method used for the analysis of metals and alloys. It is extremely rapid, since the composition can frequently be determined from the direct excitation of the sample as received. The preparation of a solution of the sample so necessary in the physico-chemical methods is thereby eliminated. The accuracy of this technique is generally lower than that of the more chemical techniques, but it is often sufficient for the rapid control analysis of production materials. For example, the Quantometer, which is an automatic spectrograph, is already well established in this country for the rapid control analysis of aluminium alloys for many alloying constituents. In large factories or establishments where the initial high cost of this equipment can be justified, there is little doubt of the labour- and time-saving value of this instrument. Spectrographic analysis is, however, a somewhat specialised technique and spectrographic methods of analysis are not included here; this review is a critical survey of the chemical and physico-chemical procedures available for the determination of major and minor amounts of many constituents of importance in non-ferrous metallurgy. The various constituents are considered below in alphabetical order for ease of reference.

#### ALUMINIUM

Volumetric methods are suitable for the determination of the aluminium content of several types of alloys containing this element in alloying amounts. It is necessary, however, to carry out a preliminary separation of the aluminium, and precipitation as its insoluble benzoate in the presence of thioglycollic acid is convenient for this purpose.<sup>8</sup> After filtration and re-solution of the precipitate in hot hydrochloric acid, an indirect volumetric procedure is available for the titration of the aluminium.<sup>9</sup> It involves the addition of an amount of a standard solution of EDTA sufficient to react with all the aluminium and to leave a slight excess. The solution is then boiled to form the aluminium - EDTA complex and the excess of EDTA is determined by titration with a standard ferric iron solution, the colour produced by ferric iron with salicylic acid being used to show the end-point of the titration. This titration is best applied when the aluminium content is known approximately so that the amount of EDTA needed can be calculated. Some practice is also necessary in recognising the end-point, because the iron - EDTA complex is more stable than the corresponding aluminium complex and fading of the iron salicylate colour occurs if the solution is allowed to stand. This titration may be improved by titrating the excess of EDTA with a standard

zinc solution, with dithizone as the indicator.<sup>10</sup> An alternative procedure involves the re-solution of the aluminium benzoate precipitate in hot ammoniacal tartrate solution, followed by the precipitation of the aluminium with 8-hydroxyquinoline. After filtration, the aluminium oxinate precipitate is dissolved in hydrochloric acid and the oxine content of the precipitate is determined by the usual bromimetric titration procedure.<sup>11</sup> This method is slightly longer than that in which EDTA is used, and therefore is less attractive for routine analysis. However, it is unnecessary to have a prior knowledge of the aluminium content and no great experience is needed to recognise the end-point. Both procedures have been applied to the analysis of copper-base alloys, including various types of brasses and aluminium bronzes. An alternative method for aluminium bronzes<sup>12</sup> involves the removal of other alloying constituents from the aluminium by mercury-cathode electrolysis before the precipitation of the aluminium with 8-hydroxyquinoline. This method is very reliable, but is less suitable for routine analysis than is that in which benzoate precipitation is used. The benzoate precipitation - EDTA titration procedure is applicable to the analysis of magnesium-base alloys.<sup>9</sup>

For the determination of small amounts of aluminium in alloys, more sensitive absorptiometric methods are available. Aluminon (ammonium aurinetricarboxylate) forms a bright red lake with aluminium in acetate solutions buffered in the range pH 4 to 5, but strict control of the solution conditions is necessary for the best results. In applying this coloured complex to the determination of traces of aluminium in lead, antimony, tin and their alloys, Luke<sup>13</sup> used a complicated separation scheme for removing the alloying constituents from the aluminium. This involved mercury-cathode electrolysis followed by extractions with a cupferron - chloroform reagent to remove such elements as titanium, zirconium, hafnium and niobium. Any vanadium remaining in the aqueous phase is formed into a complex by addition of hydrogen peroxide after the pH of the solution has been adjusted to 5, and then the aluminium is removed as its oxine complex by extraction into chloroform. The chloroform layer is heated to remove the solvent, and organic matter is destroyed by wet oxidation. The aluminon complex is then formed and the determination is completed by taking absorption measurements at a wavelength of 525 m $\mu$ . As might be expected, there is a slight loss of aluminium during these separations, and the necessary correction to be applied is determined by taking known amounts of aluminium through the same scheme. For the determination of from 0·001 to 0·01 per cent. of aluminium in gun metals, Price and Payne<sup>14</sup> found mercury-cathode electrolysis necessary for the separation of the aluminium from copper, tin, lead and so on. After this separation procedure, however, the aluminon complex is formed directly in the electrolyte, because titanium, zirconium, hafnium, vanadium and other elements that are not removed by this procedure are fortunately not constituents of this type of alloy. Since mercury-cathode electrolysis is useless for the separation of titanium from aluminium, Corbett<sup>15</sup> effected the necessary separation of the titanium in a method for traces of aluminium in titanium metal by extracting the titanium - cupferron complex into chloroform from a hydrochloric acid solution of the sample. Then, after the adjustment of the pH to 3·5, the aluminium - cupferron complex is extracted into chloroform, and these extracts are evaporated to dryness and then gently ignited to remove organic matter. The aluminium is redissolved and the determination is completed absorptiometrically as before. From the results of later work<sup>16</sup> it appears possible to improve this separation by extracting the aluminium as its oxine complex into chloroform whilst retaining the titanium in the aqueous layer as its peroxy complex. Chemical separations are not always necessary before the aluminon reagent can be applied, as shown by a direct procedure for the determination of from 0·001 to 0·01 per cent. of aluminium in zinc.<sup>17</sup> Thioglycollic acid is used as a masking agent in this method to suppress interference from iron, copper and tin.

More recently the coloured lake formed by aluminium with Solochrome cyanine has been recommended for the absorptiometric determination of small amounts of aluminium, and Bacon<sup>18</sup> uses it in a procedure for aluminium in magnesium alloys. Formation of the complex with this reagent takes place in the cold, whereas the complex with aluminon needs controlled heating for complete formation.<sup>19</sup> With Solochrome cyanine, however, a correction is necessary for the high absorption from the reagent itself, but even so the precision of the aluminium determination is in no way inferior to that obtained with aluminon. With regard to specificity there seems to be little to choose between the two reagents and in fact one reagent has no great advantage over the other. Another method of importance is based

on the pale yellow colour produced by the solution of aluminium oxinate in chloroform.<sup>20</sup> The complex is formed in alkaline solutions in the presence of cyanide to prevent possible interference from copper, nickel, cobalt and zinc, and, after extraction into chloroform, absorbancy measurements are taken at a wavelength in the region of 400 m $\mu$ . Coppins and Price<sup>21</sup> used this method for the determination of traces of aluminium in pure tin, and a similar method is recommended by Claassen, Bastings and Visser<sup>16</sup> for aluminium in phosphor bronzes and zinc-base alloys. This procedure for the zinc-base alloys is superior to the volumetric EDTA - benzoate precipitation method when only limited amounts of sample are available for analysis.

### ANTIMONY

The determination of small amounts of antimony in non-ferrous alloys presents few difficulties, since this element forms very sensitive coloured complexes and can be readily separated from other constituents, if a preliminary separation is necessary. Many absorptiometric methods are based on the strong yellow colour produced by iodoantimonite ions on the addition of excess of iodide to mineral acid solutions of tervalent or quinquevalent antimony. Hypophosphite is normally present in the solution to destroy any free iodine produced by oxidation of the iodide ions. For antimony in aluminium alloys<sup>22</sup> this complex forms the basis of a direct absorptiometric method, which is, however, only applicable to alloys low in bismuth (less than 0·03 per cent.). The absorbancy reading is a measure of antimony plus bismuth and, with alloys containing bismuth, it is necessary to determine this constituent separately and then find the antimony by difference. For traces of antimony (0·0005 to 0·02 per cent.) in pure metallic tin, Coppins and Price<sup>23</sup> combined this determination with that for arsenic. The arsenic is first removed from the sample solution as arsenious chloride, and then the antimony is separated by the Reinsch reaction in which it is deposited as Cu<sub>2</sub>Sb on copper foil. The antimony is recovered from the foil with sodium peroxide and the iodoantimonite colour is formed as before. A similar procedure is recommended for the determination of traces of antimony in copper and copper-base alloys.<sup>24</sup> The arsenic is first removed, however, by reduction to the metal with hypophosphite, followed by filtration, the Reinsch procedure being then applied to the filtrate. For copper alloys with more than trace amounts of antimony it is possible to speed the separation of this constituent by co-precipitating it with metastannic acid.<sup>25</sup> For quantitative recoveries, however, the ratio of tin to antimony must be at least 10 to 1, a condition fortunately satisfied by several types of copper-base alloys. Another very sensitive coloured complex is based on the reaction of rhodamine B with quinquevalent antimony to form an insoluble red-violet compound, which can be extracted into benzene. Ceric sulphate is suitable for ensuring the complete oxidation of the antimony. Luke and Campbell<sup>26</sup> found this complex suitable for the determination of from 0·1 to 1 p.p.m. of antimony in germanium metal and germanium dioxide, and Luke<sup>27</sup> also employed it for traces of antimony in lead samples after the preliminary separation of the major constituent as its insoluble sulphate.

This element also produces well defined polarographic steps in a variety of base electrolytes. The excellent step in a chloride base solution is unfortunately masked by copper and iron steps, which have prevented the direct polarographic determination of the antimony content of aluminium alloys. The recommended method involves a preliminary separation of the antimony as its volatile chloride and is applicable to the determination of antimony contents of less than 0·5 per cent. to within  $\pm$  0·02 per cent.<sup>28</sup> For routine analyses of samples with low bismuth contents, this method clearly cannot compete with the direct absorptiometric method. The polarographic method is also suitable for the determination of traces of antimony in metallic lead and lead alloys.<sup>29</sup> The major constituent is first separated as its insoluble sulphate and then the determination is completed by recording the anodic step for tervalent antimony from an alkaline tartrate base solution. There is apparently no interference from other constituents and the method is, therefore, specific for antimony. However, this method does not appear to have any real advantage over the rhodamine-B absorptiometric method. For antimony contents up to about 0·8 per cent. in metallic lead, Hourigan and Robinson<sup>30</sup> prefer the antimony step from the chloride base solution and their solution conditions for this determination consist of 4 to 8 M in hydrochloric acid, up to 0·03 M in lead and up to 0·002 M in antimony.

Antimony is also readily determined by volumetric procedures and such a method is reported for low alloying amounts in lead-base material (sheathing alloy).<sup>31</sup> After reduction of the antimony to the tervalent form with sodium sulphite, the solution is boiled to remove the excess of sulphur dioxide and the antimony is titrated with a standard potassium bromate solution added from a microburette. Methyl red is added to the solution near the titration end-point and the titration is stopped when the methyl red is decolourised. For satisfactory working with unknown samples, however, it is necessary to carry out a rough preliminary titration to find the approximate position of the end-point, and for this reason the volumetric method is less attractive than the polarographic method for this type of alloy. The bromate titration with methyl red as indicator is also recommended for the determination of the antimony content of white metals, which is usually high enough to permit the addition of the titrant from an ordinary burette.<sup>32</sup> Chromous sulphate is a very attractive reagent for the direct titration of antimony and a method for the determination of antimony in white metals is reported.<sup>33</sup> A hydrochloric acid solution of the sample is treated with potassium permanganate to ensure that the antimony is completely in the quinquevalent state and any excess of this reagent is decomposed by boiling. Then the titration is carried out, the end-point being determined potentiometrically. This method is more suitable for the routine analysis of white-metal samples, because of the necessity of preparing and storing the titrant under air-free conditions.

#### ARSENIC

The determination of this element presents few problems in non-ferrous analysis, because it can easily be separated from other components of a sample, and, after separation, good methods are available for the determination of both small and large amounts. The separation procedure generally used is applicable to both macro and micro quantities of arsenic and involves the distillation of arsenious chloride from a hydrochloric acid solution of the sample. The determination of small amounts of arsenic is readily accomplished by the heteropoly molybdenum-blue absorptiometric method involving the addition of ammonium molybdate to quinquevalent arsenic to form arsenomolybdate, which is then reduced to molybdenum blue with a suitable reducing agent. Rodden<sup>34</sup> reports that this method is widely applicable to the determination of trace amounts of arsenic in non-ferrous materials, including brasses, bronzes, bearing metal and so on. Coppins and Price,<sup>29</sup> however, encountered slight difficulty when applying this procedure to traces of arsenic in pure metallic tin. The difficulty arose from the appreciable amounts of hydrochloric acid collected in the receiver during the distillation procedure. The neutralisation of this free acid with ammonium hydroxide before colour development resulted in salt formation, which prevented the full development of the colour. These workers overcame this difficulty by adding a small amount of ferric iron to the acid distillate, followed by ammonium hydroxide to make the solution alkaline. The arsenic is completely co-precipitated with the ferric hydroxide under these conditions and, after filtration, the precipitate is dissolved in a controlled amount of acid. An alternative method for arsenic in copper-base alloys and pig lead employs the preliminary separation of the arsenic by precipitation, the arsenic being reduced to the metallic state with hypophosphorous acid.<sup>35</sup> This procedure may be of advantage in routine analysis unless several distillation units are readily available.

The analysis of germanium metal and germanium dioxide for traces of arsenic has assumed importance in recent years because of the use of these materials in transistor manufacture. Luke and Campbell<sup>26</sup> have developed a method for the determination of from 0·1 to 1 p.p.m. of arsenic. Separation of the arsenic by distillation proved unsuitable in this work because of the volatility of the germanium chloride, but these workers successfully applied solvent extraction to this problem. In the recommended method the arsenic is isolated by extractions with diethylammonium diethyldithiocarbamate in chloroform from a 2 N hydrochloric acid solution also containing oxalic acid. In spite of the strong complexation of the germanium with oxalic acid, a small amount of this constituent accompanies the arsenic in the extraction procedure. After the removal of chloroform from the combined extracts, therefore, organic matter is destroyed by wet oxidation and the germanium is removed as its volatile chloride whilst the arsenic is maintained in its quinquevalent state. The arsenic is then converted into its molybdenum-blue complex and the determination completed absorptiometrically. Payne<sup>36</sup> prefers to complete the determination of very small amounts of arsenic separated

from germanium by this solvent-extraction method by a modified Gutzeit test in which the hydrogen is generated electrolytically from a zinc-plated cathode. The activation method is applicable to the determination of arsenic contents of less than 0·1 p.p.m. in this type of material. In fact, by using the Harwell pile, Smales and Pate<sup>37</sup> succeeded in determining arsenic contents of 0·01 p.p.m. in germanium dioxide.

Volumetric methods are available for the determination of larger amounts of arsenic. One suitable method involves the direct titration of arsenious acid with a standard solution of iodine, starch being used as the indicator.<sup>38</sup> Since the reaction in this titration is reversible, it is necessary to have an excess of sodium bicarbonate in solution to destroy the hydriodic acid as it is formed. This titration is directly applicable to the distillate obtained in the separation of arsenic from the other constituents of a sample as arsenious chloride. In a method for the determination of less than 0·1 per cent. of arsenic in copper-base alloys, the above procedure is applied after the preliminary separation of the arsenic by co-precipitation on ferric hydroxide.<sup>32</sup> For greater arsenic contents of up to about 1 per cent. in this type of alloy, the distillation procedure is carried out directly on a solution of the sample, the temperature of the vapours in the distillation flask being allowed to reach a value of 105° C. Then the arsenic in the distillate is determined by titration with a standard solution of potassium bromate, with methyl orange as indicator, preferably added near the end-point of the titration.<sup>32</sup>

### BERYLLIUM

Small amounts of this element are determined absorptiometrically. One method makes use of the red-brown lake formed by beryllium with *p*-nitrophenylazo-orcinol. The dye is yellow in basic solutions, but when it is added to an alkaline beryllium solution, a red-brown lake is produced. The alkalinity of the final solution must be controlled over a fairly narrow range for the best results and buffering with a borate buffer is recommended. The Beer-Lambert law is not strictly obeyed by this complex, but reproducible results can be obtained by careful control of the solution conditions. This method is recommended by Osborn and Stross<sup>22</sup> for the determination of the beryllium content of aluminium alloys. The sample is dissolved in sodium hydroxide and then the coloured lake is formed after the removal of any insoluble matter with the assistance of a centrifuge. This method is also used in a procedure for the determination of the beryllium oxide content of beryllium metal.<sup>39</sup> The beryllium metal is completely volatilised from the sample with hydrogen chloride gas at a temperature of 600° C. Then the residue, consisting of beryllium oxide, is treated with sulphuric acid and heated to effect complete solution. The beryllium is separated from this solution by co-precipitation on aluminium hydroxide and, after filtration and washing, the precipitate is dissolved in sodium hydroxide and the coloured lake is formed. In a method for the direct determination of the beryllium content of copper - beryllium alloys, Luke and Campbell<sup>40</sup> made use of the coloured lake formed by beryllium with aluminon. Interference from other alloying constituents is prevented by the inclusion of EDTA in the final solution. This method is possible because of the negligible aluminium content of this type of material and it is only recommended for the rapid control analysis of production samples.

Adam, Booth and Strickland<sup>41</sup> have criticised the absorptiometric methods for beryllium wherein coloured lakes are used, because of the rigorous control of conditions necessary to ensure reproducible lake formation. These workers recommend a method involving the use of acetylacetone, which forms a definite molecular species with beryllium. This complex is first used for the separation of the beryllium from other sample constituents. It is extracted into chloroform from sample solutions containing EDTA and the pH is adjusted to between 7 and 8. The extracts are combined and organic matter is destroyed by wet oxidation. The beryllium - acetylacetone complex is re-formed in this solution and extracted into chloroform. The chloroform layers are combined, diluted to a defined volume and then washed with 0·1 N sodium hydroxide solution. A 1-cm quartz cell is filled with the chloroform extract after it has been passed through a dry filter-paper, and absorbancy measurements are made at a wavelength of 295 m $\mu$ .

Gravimetric methods are available for the determination of this element when present as a major constituent. The method employed for the determination of the beryllium content of beryllium metal and beryllium salts involves the precipitation of the beryllium as its hydroxide followed by ignition to beryllium oxide.<sup>39</sup> With this method, however, it is necessary to remove certain constituents, if present, before the precipitation with ammonium

hydroxide. Silica is readily removed by dehydration in the usual way. Iron and aluminium are separated by precipitating their oxinates at pH 4.3 to 4.6; alternatively, these oxinates can be extracted into chloroform. After the destruction of organic matter in the sample solution by wet oxidation, beryllium hydroxide is precipitated by the addition of ammonium hydroxide. Electrolysis by means of a mercury cathode is a useful technique for separating many elements from beryllium before the precipitation of this element as its hydroxide. A more attractive gravimetric method involves the precipitation of the beryllium as beryllium ammonium phosphate and subsequent ignition to beryllium pyrophosphate.<sup>42</sup> This method gives almost four times as much mass to weigh per equivalent of beryllium content as the beryllium oxide method. The precipitation can also be carried out in the presence of EDTA, which complexes many elements and prevents their interference. The beryllium precipitate is formed in solutions of pH 5.5 by the addition of diammonium hydrogen phosphate.

### BISMUTH

Absorptiometric methods are suitable for the determination of small amounts of this constituent of non-ferrous alloys. Very sensitive coloured complexes are given by bismuth with dithizone and with iodide ions, but the less sensitive yellow colour obtained with thiourea is far more specific for the determination of this element. Stross and Osborn<sup>22</sup> used the thiourea complex in a direct method for bismuth in aluminium alloys, interference from iron being prevented by reduction to the ferrous state with hydrazine. Antimony also forms a weakly yellow coloured complex with thiourea, but interference is eliminated in this method by the preferential complexation of the antimony with fluoride ions. In a procedure for the determination of traces of bismuth in tin metal, Coppins and Price<sup>21</sup> remove the tin by volatilisation as its volatile halide. There is no loss of bismuth in this separation procedure provided that the solution contains perchloric acid. The thiourea complex is formed in the final solution. This method is also applicable to the analysis of tin-base white metals, the antimony in the sample being removed with the tin in the volatilisation procedure. Hall<sup>43</sup> uses the thiourea complex for the analysis of pure lead for traces of bismuth. The prior separation of the bismuth from the lead is effected by co-precipitating the bismuth on manganese dioxide. A more attractive method of separating small amounts of bismuth from lead is contained in a recent paper by Fiander,<sup>44</sup> 9-methyl-2:3:7-trihydroxy-6-fluorone being used as the precipitant from a nitric acid solution of the sample. After filtration, the precipitate is dissolved in sulphuric acid and then evaporated to fumes of this acid. This determination is finally completed by using the yellow iodo complex for bismuth, and it is claimed to be suitable for the analysis of refined lead, antimonial lead, lead-tin solders and so on. The iodo complex is also used in a suitable method for the determination of bismuth in copper-base alloys.<sup>45</sup> On the addition of potassium iodide to a solution of the sample to form the bismuth complex, a precipitate of cuprous iodide is formed and free iodine is liberated. The iodine colour is discharged with hypophosphorous acid and the cuprous iodide removed by filtration. Then the bismuth content is determined by measuring the absorbancy of the filtrate. This method is very sensitive and can be applied to almost all copper-base alloys other than those containing large amounts of nickel.

Bismuth produces polarographic steps in several base electrolytes, and these are suitable for analytical purposes. In a method for the determination of traces of bismuth in pure tin metal,<sup>46</sup> the preliminary separation of the major constituent is necessary and the bismuth step is then recorded from a tartrate base electrolyte. The copper, lead, cadmium and zinc contents of the sample can also be determined polarographically in this solution and the polarographic method is, therefore, more useful than the absorptiometric method when the complete analysis of the sample is required. In a procedure for bismuth in tin-lead solders,<sup>47</sup> no chemical separations are necessary and this constitutes an improvement on the corresponding absorptiometric method. Interference from tin is prevented by the inclusion of EDTA in the base solution in addition to citrate ions; the final solution has a pH value of 9. The copper content of the solder can be found simultaneously with the bismuth. For the polarographic determination of bismuth in refined lead,<sup>29</sup> it is necessary to remove the major constituent as its insoluble sulphate before the bismuth step is recorded from a tartrate base solution of pH 3.7. The polarographic method is more useful than the absorptiometric methods when the complete analysis of the sample is required, since traces of iron, copper, cadmium and zinc can be determined in the same final solution.

The most suitable procedure for bismuth when present as a major alloying constituent involves titration with EDTA. Several indicators are available for the direct titration and moreover, since the bismuth - EDTA complex is readily formed in solution having low pH values, this determination can be carried out in the presence of many other elements without interference. Schwarzenbach<sup>48</sup> and later Cheng<sup>49</sup> used potassium iodide as indicator, the titration with EDTA being carried out until the bismuth iodide colour is just discharged. The sensitivity of this end-point is dependent on the potassium iodide concentration and the pH of the solution. The yellow colour given by bismuth with thiourea is also suitable in titrations with EDTA.<sup>50</sup> Pyrocatechol violet<sup>51</sup> is another indicator available for this titration, a reddish colour being produced on the addition of a few drops of a 0·1 per cent. solution to a bismuth solution in the pH range from about 1·0 to 3·0. At the end-point of the titration with EDTA the colour of the solution changes to yellow. The following elements can be present without causing interference: Pb, Cd, Cu, Ag, Al, Zn, Co, Ni, Mn, Ca, Mg and U. Milner and Edwards<sup>52</sup> found this titration very convenient for the determination of the bismuth content of bismuth - uranium and bismuth - uranium - thorium alloys, the thorium being preferentially complexed with sulphate ions.

### BORON

Methods for the determination of microgram amounts of boron in certain materials used in atomic-energy work have been extensively investigated in recent years because of the high thermal-neutron capture cross-section of boron atoms. The absorptiometric method used in the United Kingdom project has been developed at the Woolwich laboratory, formerly of the Chemical Inspectorate, Ministry of Supply, now of the U.K.A.E.A. Research Group, by Strickland, Oliver, Allan, Strachan and Spicer,<sup>53</sup> and it is based on the work of Naftel,<sup>54</sup> who measured the red colour produced on evaporating to dryness a mixture of curcumin, oxalic acid and hydrochloric acid with boric acid in aqueous alcoholic medium. This method is extremely sensitive, but careful control is necessary to obtain reproducible results. Spicer and Strickland<sup>55,56</sup> have established that the coloured product contains boric acid in chemical combination and in fact, under Naftel's conditions two distinct complexes of the following types are formed: (i) rubrocurcumin, which is composed of a curcumin residue, one boron atom and one oxalate radical, and (ii) rosocyanine, which consists of two curcumin residues and one boron atom. The absorption spectra for these two complexes are similar in the range 400 to 600 m $\mu$ , and their absorbancies at a wavelength of 550 m $\mu$  for equal amounts of boron are in the ratio of 1·64 to 1 (rosocyanine to rubrocurcumin).

The coloured complex is normally formed after the selective separation of the boron from the other constituents of the sample by distillation as methyl borate. The distillate is collected in a platinum dish, sodium hydroxide - glycerol solution is added and, on completion of the distillation, methanol and water are removed from the distillate by gentle heating until a glycerol residue remains. The glycerol is in fact used to prevent excessive loss of boron as its methyl ester during this evaporation. It unfortunately causes interference in the subsequent colour reaction and must itself be fumed off and the residue ignited under controlled conditions. A 4 per cent. loss of boron is reported during the evaporation and ignition stages, but there is some evidence that suggests that on occasions this loss may, in fact, be greater. In the development of the boron - curcumin colour on the dry sodium hydroxide residue, the temperature and humidity of the ambient air must be controlled, since they influence the final colour intensity. Suitable control is effected by floating the platinum dish containing the dry sodium hydroxide residue together with a reagent solution consisting of curcumin, oxalic acid and hydrochloric acid in aqueous ethanol on the surface of a water bath controlled between 55° and 59° C. The temperature of the air above the bath as measured by a thermometer shielded from direct radiation and clamped vertically with its bulb 2 inches above the surface of the water should exceed 35° C. The air temperature is conveniently maintained at such a value by placing the water bath symmetrically upon a hot-plate in a semi-enclosed space so that a column of warm air surrounds the bath. It is necessary to protect the surface of the bath from direct sunlight or radiant heat and this is achieved by placing a sheet of glass or plastic material about 12 inches above the bath. This screen also gives additional stability to the air conditions. Further information on this method is given in some detail, because it has not been generally available until recently.

## SPECIAL REAGENTS—

*Glycerol-sodium hydroxide solution*—Dissolve 1 g of AnalaR sodium hydroxide and 3 ± 0.3 ml of pure glycerol in 100 ml of redistilled water.

## No. 1 curcumin colour reagent—

(i) *Stock aqueous ethanol*—Fill a 1-litre calibrated flask to the mark with absolute ethanol and pour off 30 ml. Add 35 ml of distilled water to the contents of the flask and mix well. Note the temperature and adjust it to between 15° and 20° C. Measure the specific gravity with a clean hydrometer calibrated in the range 0.7600 and 0.8200 at 60° F. Add further small quantities of distilled water until the specific gravity (corrected for temperatures above 15° C by adding 0.0008 per degree) is 0.809 ± 0.0005.

(ii) *Colour reagent*—Transfer about 300 ml of the aqueous ethanol from the flask to a clean measuring cylinder and then add 15.0 g of AnalaR oxalic acid dihydrate to the aqueous ethanol left in the flask. Also put into the flask 15.0 ml of AnalaR hydrochloric acid, sp.gr. 1.16, from a burette and 85 ml of distilled water. When all the oxalic acid is in solution, add 1.00 g of recrystallised curcumin and make the volume of the solution up to about 950 ml with the stock aqueous ethanol previously removed from the flask. Dissolve the curcumin by periodic shaking. When solution is complete or no more than a trace of solid remains, cool to 20° C and adjust the volume to the 1-litre mark with the stock aqueous ethanol.

No. 2 curcumin colour reagent—This reagent is for the determination of traces of boron (less than 5 µg) and is prepared by the same method as the No. 1 reagent, but from 15 g of AnalaR oxalic acid, 30 ml of AnalaR hydrochloric acid, sp.gr. 1.16, 75 ml of water and 0.35 g of recrystallised curcumin.

## PROCEDURE—

To the methanolic distillate containing less than 30 µg of boron in a 3 or 3½-inch diameter platinum dish, add 0.5 to 0.6 times its volume of distilled water and 2 ml of the glycerol-sodium hydroxide solution. Place the platinum dish upon a water bath maintained at 85° to 90° C and evaporate the solution to dryness. (Note 1.) Heat the dish at a temperature between 150° and 250° C on a hot-plate to remove most of the glycerol. Heat slowly and take 10 to 15 minutes over the process. Then heat gently over a bunsen flame to remove the last traces of glycerol and finally raise the temperature to a dull red heat, maintaining the dish at this temperature for about half a minute. (Note 2.) For normal determinations add 10.0 ml of No. 1 curcumin reagent from a pipette, rinsing the sides of the dish with the liquid as it enters. Float the dishes upon the surface of the "colour development" bath and, from time to time during the first 5 minutes of heating, gently swirl the liquid in the dish to complete the solution of the residue. Afterwards leave undisturbed until the contents of the dish are dry. Heat for a further few minutes until most of the hydrochloric acid vapour has been driven off (at least 3 minutes should be given from the time of going dry, but no harm is done if heating is prolonged up to at least 45 minutes). Cool the dish and add about 10 ml of industrial methylated spirit (approximately 90 per cent. of ethanol, 5 per cent. of methanol and 5 per cent. of water) and allow the coloured complex to dissolve, using a rubber-tipped glass rod to assist complete solution. (Note 3.) Transfer the solution to a 50-ml calibrated flask and rinse the dish thoroughly with industrial methylated spirit, sufficient being used to extract all coloured matter from the dish and to dilute the solution to the calibration mark. Mix the solution and filter a portion through a small dry Whatman No. 1 filter-paper into a suitable absorptiometer cell. Measure the absorbancy of the solution with a Spekker absorptiometer, using a mercury-vapour lamp, H503 heat-resisting filters and Ilford No. 605 filters. Correct this value for that of a blank determination carried out on all the reagents, using the same quantities and identical conditions as in the test determination. Refer the corrected absorbancy to a calibration graph to determine the number of micrograms of boron present in the distillate.

## NOTES—

1. At this stage there is a slight loss of boron, which is nearly constant at 4 per cent. and cannot be prevented by any practicable procedure. For the most accurate work, therefore, a correction of 4 per cent. should be added to the final boron figure.

2. If fusion should occur during the heating process, the fused salt should be dissolved in the bare minimum of water, which is prevented as far as possible from creeping up the sides of the dish. This

solution is then evaporated gently to dryness on the water bath and the residue is dried for a few minutes at about  $100^{\circ}\text{C}$  before colour development.

3. Extraction with this grade of methylated spirit is often convenient and economical, but pure ethanol may be used provided that it contains not more than 25 or less than 5 per cent. of water by volume.

#### CALIBRATION PROCEDURE—

Prepare a standard boron solution by dissolving 1.43 g of AnalaR boric acid in water and diluting to a volume of 250 ml. For use, dilute 2.5 ml of this solution to 250 ml with water so that 1 ml is equivalent to 10  $\mu\text{g}$  of boron. Add the standard quantities of boron shown below to 3 or 3½-inch platinum dishes each containing 2 ml of the glycerol - sodium hydroxide solution. Then add 4 ml of pure methanol to each dish and evaporate each solution at a low temperature (about  $70^{\circ}\text{C}$ ) until the bulk of the methanol is removed and finally to dryness on a water bath maintained at  $85^{\circ}$  to  $90^{\circ}\text{C}$ . Continue the colour development and take absorbancy measurements as described above. For 5.0, 7.5, 10.0, 12.5 and 15.0- $\mu\text{g}$  amounts of boron, measure the absorbancies with 1 and 2-cm cells. Using the same cells, measure the reagent blank (2 ml of glycerol - sodium hydroxide reagent and 4 ml of methanol only) and plot the corrected absorbancy values against the boron content to produce linear calibration graphs.

This method has been applied to the determination of traces of boron in uranium metal<sup>57</sup> and graphite.<sup>58</sup>

#### OTHER METHODS—

The recently published methods<sup>59</sup> used in French Atomic Energy Establishments for the determination of traces of boron also uses the curcumin colour reaction. The coloured complex is formed, however, in conditions recommended by Philipson,<sup>60</sup> in which trichloroacetic acid is used instead of oxalic acid, and this procedure appears to be simpler than that used in this country. In the method for the analysis of beryllium oxide and uranium, the boron is first separated from other constituents of the sample by extraction into chloroform as tetraphenylarsonium fluoroborate and the solvent phase is transferred to a platinum dish. After the addition of 15 drops of 0.1 N sodium hydroxide and one drop of phenolphthalein, the dish is placed under a special heater and the solution is evaporated to dryness. Solution of the residue is effected in 1 ml of *N* trichloroacetic acid and, after a waiting period of 10 minutes, 1 ml of 95 per cent. ethanol is added to this solution. The contents of the dish are then thoroughly mixed and 1 ml of a 0.125 per cent. solution of curcumin in ethanol is added. The coloured complex is formed by placing the dish in an oven at a temperature of  $105^{\circ} \pm 1^{\circ}\text{C}$  for a period of  $60 \pm 3$  minutes and the residue is then extracted with ethanol. This solution is diluted to a volume of 25 ml and the boron content is found from absorbancy readings taken at a wavelength of 540 m $\mu$  in 1-cm cells.

For the determination of milligram amounts of boron the volumetric method based on the formation of mannitoboric acid and titration of this complex with standard sodium hydroxide is widely used. This method is suitable for the determination of the boron content of boron metal<sup>61</sup> after fusion of the sample with sodium carbonate and solution of the melt in diluted hydrochloric acid. The pH of this solution is adjusted to a value in the range 5 to 5.5 by the addition of sodium hydroxide and, after warming to  $60^{\circ} \pm 5^{\circ}\text{C}$ , carbon dioxide is removed by the passage for 30 minutes of air that has been purified by passing through concentrated sulphuric acid and Ascarite. The sample solution is then allowed to cool and is diluted to a suitable volume. An aliquot containing about 60 mg of boron is transferred to a 600-ml beaker, this solution is diluted to a volume of about 250 ml with water free from carbon dioxide and its pH is adjusted to a value of 6.3 by the use of carbonate-free 0.05 N sodium hydroxide. On the addition of mannitol to this solution, the pH decreases markedly, owing to the formation of mannitoboric acid, and the titration procedure consists in adding standardised 0.1 N sodium hydroxide from a burette until the initial pH value of 6.3 is restored. The sodium hydroxide solution is preferably standardised against pure fused boric oxide, the amount taken being adjusted to give approximately the same titre as the sample solution. By this method of standardisation the standard alkali solution is expressed directly in terms of boron.

In the analysis of boronised iron, nickel, cobalt and copper samples, Bush and Higgs<sup>62</sup> used mercury-cathode electrolysis to isolate the boron before titrating the mannitoboric acid complex.

### CADMIUM

This element generally occurs in non-ferrous alloys either as a minor alloying constituent or as a trace impurity. Polarographic methods are the most convenient for the determination of this element, since it gives well defined steps in many different base electrolytes, including acid and alkaline solutions. Alloying amounts of cadmium are present in certain types of copper-base alloys and a polarographic method is available for this determination.<sup>58</sup> The well defined step from an alkaline cyanide base solution is used, since under these conditions the copper is so strongly complexed with cyanide that no interference is encountered. Slight difficulty occurs with samples containing manganese, which is gradually precipitated from the alkaline solution, and with alloys containing more than 1 per cent. of this constituent, it is necessary to include ammonium citrate in the final solution to repress its precipitation. Alloying amounts of cadmium are found in silver-base alloys and the amount of this constituent can be determined directly by recording the step from an ammonium hydroxide - ammonium chloride base solution.<sup>63</sup> There is no interference from silver under these conditions.

For the determination of trace amounts of cadmium (less than 0.005 per cent.) in zinc-base Mazak alloys, a direct polarographic method is applicable to a hydrochloric acid solution of the sample after the preliminary reduction of ferric iron with hydrazine hydrochloride.<sup>64</sup> This direct determination is possible because the copper, lead and tin contents are also very small. However, difficulty occurs with samples containing indium owing to the close proximity of the indium and cadmium steps in the chloride base solution and this is best overcome by using a cathode-ray polarograph, which gives a better resolution than the conventional polarograph.<sup>65</sup> The determination of the cadmium content of aluminium alloys is only very occasionally required, but when it is needed a polarographic method is the most suitable.<sup>66</sup> This is not a direct procedure because of the presence of alloying amounts of copper, which must be removed before the cadmium step is recorded by conventional polarography. In the recommended method copper and lead are removed from a nitric acid solution of the sample by electrolytic deposition on platinum electrodes. Then the cadmium step is recorded after the reduction of iron with hydroxylamine hydrochloride. This procedure is applicable to all types of aluminium alloys, but it should be possible to simplify this determination by the use of square-wave polarography.<sup>67</sup> The determination of the cadmium content of tin-base white metals is readily accomplished by conventional polarography after the removal of the tin and the antimony as their volatile halides; the cadmium step is recorded from an ammonium chloride - ammonium hydroxide base electrolyte.<sup>47</sup> For alloys with high copper contents the preliminary removal of this constituent by the precipitation of cuprous iodide is also necessary before the cadmium step is recorded. This determination is considerably simplified by the use of square-wave polarography.<sup>67</sup> After the removal of the tin and antimony, the cadmium peak is recorded directly for the resultant solution in the presence of a chloride base electrolyte. There is no need to remove the copper from solution and, in fact, the copper and lead contents of the sample can be determined at the same time. For traces of cadmium in pure lead metal, the polarographic method involves solution of the sample in nitric acid, followed by precipitation of the lead by the controlled addition of sulphuric acid.<sup>68</sup> After the removal of the precipitate, the solution is made 1.5 M in ammonium sulphate, 0.1 M in ammonium carbonate, 0.5 M in ammonium hydroxide and 0.005 per cent. in gelatin, and then the cadmium step is recorded. This method is also suitable for the determination of the copper, nickel and zinc contents of the sample, in addition to the cadmium, provided that the polarogram is recorded from zero applied voltage to record the copper step.

Absorptiometric methods are available for the determination of trace amounts of cadmium in various materials. They are based on the coloured complex formed by cadmium with dithizone, which is separated by solvent extraction. The complete procedure consists of several extractions. In a preliminary extraction the cadmium is separated with a 0.1 per cent. solution of dithizone in carbon tetrachloride from an ammoniacal solution of the sample (pH 8 to 11), containing a hydroxy acid, if necessary, to prevent the formation of a hydroxide

precipitate. The following metals, if present, separate into the organic layer with the cadmium: Bi, Co, Cu, Pb, Hg, Ni, Ag, Th and Zn. The combined dithizone extracts are washed free from alkali and then extracted with small volumes of 0·01 M hydrochloric acid. The cadmium passes into the acid layer along with bismuth, lead and zinc. Final separation is effected by making the combined acid layers approximately 5 per cent. alkaline with sodium hydroxide solution and then re-extracting with the carbon tetrachloride solution of dithizone. The resulting extract is pink owing to the cadmium in the sample, and the amount of this constituent is found from absorbancy measurements. This procedure is employed for the determination of traces of cadmium in lead,<sup>69</sup> and a slightly modified form is used in the analysis of tin.<sup>21</sup> In this method copper and iron are first removed by extraction of their cupferrates with chloroform and, after the destruction of any traces of cupferron in the aqueous solution with bromine water, the cadmium is precipitated as the brucine-cadmium iodide complex. The extraction of this complex into chloroform effects the separation of the cadmium from nickel and zinc. The chloroform layer is extracted with dilute hydrochloric acid and the cadmium - dithizone complex is formed as before, after making the solution alkaline with sodium hydroxide. It is possible to determine only the cadmium content of the sample with this type of absorptiometric procedure. The polarographic methods are potentially more useful, therefore, when the complete analysis of lead and tin samples is required.

### CHROMIUM

The determination of small alloying amounts of this element is readily accomplished by absorptiometric methods based on the oxidation of the chromium to its sexavalent state. This oxidation can be effected by any one of several methods, the most common involving fuming the sample with perchloric acid or boiling the sample solution with ammonium persulphate in the presence of silver ions. With samples also containing manganese, the oxidation procedure invariably produces permanganate ions. Interference from this constituent is readily removed, however, by the selective reduction of the permanganate ions with sodium nitrite in the presence of urea. In an absorptiometric method for chromium in nickel-base alloys,<sup>70</sup> the chromium is oxidised by fuming with perchloric acid in the presence of phosphoric acid. Although manganese is only partially oxidised under these conditions, it is still necessary to discharge the permanganate colour with sodium nitrite. After measurement of the absorbancy of the oxidised chromium solution, the chromium is reduced with sulphurous acid and the absorbancy is re-measured, the difference in absorbancy being proportional to the chromium content. For the determination of traces of chromium, the absorptiometric method is made more sensitive by the production of the violet - red coloration with diphenylcarbazide. Ferric iron gives a yellow colour with this reagent, but this effect is considerably diminished by the addition of phosphoric acid to the solution. A solution of diphenylcarbazide in acetone is preferable to those in ethanol or acetic acid, since it is more stable. In the author's experience<sup>71</sup> this procedure is suitable for the determination of chromium in lithium metal and beryllium salts and should, moreover, be widely applicable to non-ferrous materials.

Polarographic methods are also available for the determination of small alloying amounts of chromium, since a well defined step with an  $E_1$  value of -0·85 volt against the S.C.E. is produced by chromate ions from a sodium hydroxide base solution.<sup>72</sup> This step is used in a method for the determination of 0·1 to 0·5 per cent. of chromium in aluminium alloys.<sup>73</sup> For alloys containing less than 0·25 per cent. of copper, the method is direct, involving solution of the sample in a mixture of hydrochloric and nitric acids, followed by evaporation to fumes of sulphuric acid. Then the chromium is oxidised by boiling with ammonium persulphate and the hot solution is added dropwise to sodium hydroxide solution. After boiling, any precipitate is separated and the polarogram is recorded on a portion of the filtrate. For samples with greater copper contents, a preliminary separation of this element is carried out by electrolysis. The same polarographic step is used for the determination of alloying amounts of chromium in titanium alloys, after the removal of the titanium by hydrolysis.<sup>74</sup>

Macro amounts of chromium are readily determined by volumetric procedures. As with the physico-chemical methods, it is necessary to oxidise the chromium to its sexavalent state; then the solution is cooled and a standard ferrous sulphate solution is added from a burette until the solution changes colour from yellow to green. The excess of ferrous sulphate

is determined by titration with a standard potassium permanganate solution until a faint pink colour is produced, persisting for at least 1 minute. Vanadium is the only element to cause interference; it slowly re-oxidises and causes a fading end-point in the permanganate titration. Vanadium is not, however, a normal alloying constituent of non-ferrous alloys. This procedure is suitable for the determination of chromium contents greater than 1 per cent. in aluminium alloys after the oxidation of the chromium with sodium bismuthate.<sup>75</sup> The method is claimed to be accurate to  $\pm 0.015$  per cent. for chromium contents from 1.0 to 5.0 per cent. and to  $\pm 0.03$  per cent. for amounts greater than 5.0 per cent.

### COBALT

Small amounts of cobalt are readily determined by absorptiometric methods based on the coloured complex formed by this element with nitroso-R salt. This complex is formed in an acetate buffer of pH 5.5 on boiling the solution for about 45 seconds. Excess of the reagent and the complexes formed with other heavy metals are decomposed by boiling with nitric acid for about 1 minute, and the cobalt content of the sample is found from the absorbancy of the solution measured at a wavelength of 510 m $\mu$ . The method is essentially specific for cobalt, and it has been used for the determination of this element in aluminium alloys,<sup>76</sup> tin metal<sup>21</sup> and beryllium salts.<sup>77</sup> The absorptiometric procedure is more suitable for general metallurgical analysis than the polarographic procedure, in spite of the fact that cobalt gives well defined polarographic steps. The step for the reduction of Co<sup>3+</sup> to Co<sup>2+</sup> is potentially more useful and subject to less interference than that for the reduction of Co<sup>2+</sup> to the amalgam. However, this involves the prior oxidation of the cobalt and the removal of the excess of oxidant before the step is recorded.<sup>72</sup>

Volumetric methods are available for the determination of alloying amounts of this element. One useful method is based on the oxidation of cobaltous ions in ammoniacal solution by the addition of a standard potassium ferricyanide solution in slight excess, the amount in excess being titrated with a standard cobalt solution.<sup>78</sup> The end-point is determined potentiometrically, when there is a change in potential of about 200 mV. When citrate ions are included in the sample solution to prevent the formation of hydroxide precipitates, this titration is applicable in the presence of iron, nickel, copper and so on. Yardley<sup>79</sup> has formulated the best conditions for obtaining for cobalt results of the highest accuracy by this procedure. In alloy analysis Milner and Macara<sup>80</sup> found this titration eminently suitable for the direct determination of the cobalt content of uranium - cobalt alloys, whilst Chirnside, Cluley and Proffitt<sup>81</sup> used it in the analysis of nickel - cobalt - iron alloys used in glass-to-metal seals. Recently this titration has been modified by the replacement of the ammonia with ethylenediamine.<sup>82</sup> By this means the potential break at the end-point is increased to about 600 mV, and this improved sensitivity at the end-point has resulted in the development of direct titrations. Diehl and Butler, for example, used a direct titration for the determination of the cobalt content of beryllium - cobalt bronzes. For the analysis of silver-bearing bronzes they found the back-titration procedure more suitable.

### COPPER

The coloured complex formed by copper with sodium diethyldithiocarbamate is very sensitive and suitable for the absorptiometric determination of this element. Although copper reacts with sodium diethyldithiocarbamate in either acid, neutral or alkaline solution, the ammoniacal conditions are the most important, since they inhibit interference from nickel. Under these conditions, however, the tendency for the copper complex to be precipitated increases with the ammonia concentration. Because of the low solubility of the complex, it is necessary either to hold it in colloidal suspension with gum arabic or to extract it into an organic solvent. In routine analysis the first method is usually employed because of its simplicity, and it is used in procedures for copper in aluminium alloys<sup>22,83</sup> and magnesium alloys.<sup>84</sup> The extraction of the copper complex into carbon tetrachloride is used in methods for the determination of this constituent in tantalum,<sup>85</sup> uranium<sup>86</sup> and beryllium salts.<sup>87</sup> In the first case the copper diethyldithiocarbamate complex is formed in the presence of tartrate to maintain the tantalum in solution, whereas with uranium metal the major constituent is kept in solution as its carbonate complex. In recent work Cluley<sup>88</sup> prefers to maintain nickel, iron, cobalt, etc., in solution as their soluble EDTA complexes during the formation and extraction of the copper diethyldithiocarbamate complex. With this procedure it

is possible to determine the copper content of lead-base alloys and iron - nickel - copper alloys very readily. For traces of copper in pure tin, Coppins and Price<sup>61</sup> prefer the coloured complex produced by copper with rubeanic acid, with gum arabic as the stabiliser. The preliminary removal of the tin as its volatile bromide is necessary in this method, which is suitable for copper contents in the range 0.002 to 0.04 per cent.

Although polarographic methods are available for the determination of the copper content of many non-ferrous alloys, these methods offer no outstanding advantages over the absorptiometric methods, except in a few cases. The polarographic method is useful for the determination of traces of copper in high-purity zinc and Mazak alloys.<sup>64</sup> The copper step is recorded directly for a solution of the sample in hydrochloric acid after the reduction of iron to the ferrous state with hydrazine hydrochloride. The lead, tin and cadmium contents can also be determined in this solution of the alloy. In a method for traces of copper in pure tin, the copper step is recorded from a tartrate base solution after the preliminary removal of the main constituent as its volatile bromide.<sup>65</sup> This method is more useful than the absorptiometric method when a full analysis of the sample is needed, since the bismuth, lead, cadmium and zinc contents can be determined in the same solution. For samples in very limited supply, this determination is readily carried out with the square-wave polarograph. Ferrett and Milner<sup>67</sup> applied this instrument to the determination of the copper, lead, indium and zinc contents of a pure tin sample, using a total sample weight of 50 mg. In the analysis of tin - antimony - lead solders for copper, Faucherre and Souchay<sup>67</sup> prevented interference from the major constituents by incorporating EDTA in the citrate base solution of pH 9. A polarographic method for traces of copper in refined lead involves the precipitation of the lead as its sulphate, the polarogram being finally recorded from a tartrate base solution.<sup>68</sup> It is possible to determine the iron, bismuth, cadmium and zinc contents of the sample simultaneously, and this method is more suitable, therefore, when the complete analysis of the sample is required.

The determination of this element when present as a major alloying constituent is conveniently carried out by electro-deposition, the copper being plated as metal on to a weighed cylindrical cathode from a weakly acid solution of the sample. This method is accurate. The plating can be carried out from a sulphuric acid or a nitric acid solution or one containing a mixture of these acids. It is frequently directly applicable to acidic solutions of non-ferrous alloys, since tin and antimony are the only constituents that must be removed before the electrolysis. As mentioned in the introduction, the potential of the cathode must be controlled for the deposition of copper from hydrochloric acid solutions.<sup>3</sup> After the deposition of the copper from solutions of copper-base alloys by this method, the determination of many other alloy constituents can be readily carried out by either polarographic<sup>69</sup> or absorptiometric methods.<sup>3</sup>

#### GALLIUM

The determination of the gallium content of alloy solutions is greatly simplified because of the extractability of this element from chloride-containing solutions with organic solvents. Although diethyl ether is the usual solvent for this extraction, many other organic solvents are just as suitable.<sup>90</sup> After the extraction of the gallium from the organic layer back into water, the determination of the gallium content is readily accomplished by direct titration with EDTA, with gallocyanine as the indicator.<sup>91</sup> This procedure is suitable for amounts of gallium ranging from 0.25 mg to at least 50 mg, and it should find general application in alloy analysis. Ferric iron unfortunately interferes with this method, since it is extracted in the solvent-extraction process and also consumes EDTA in the titration procedure. For alloys containing this constituent, therefore, a gravimetric method involving the precipitation of the gallium as its camphorate appears to be more suitable.<sup>90</sup> When the iron is in the ferrous state, it does not interfere in the precipitation of gallium camphorate and the determination can then be completed by filtration through a tared No. 4 sintered-glass crucible, followed by drying at 110° C and weighing. In favourable circumstances the gallium content can be determined without any preliminary chemical separation, and the author found this to be true in the analysis of uranium - gallium binary alloys.<sup>92</sup> Uranyl ions do not form complexes with EDTA in solutions having pH values of less than about 4, so that conditions can be chosen in which the gallium preferentially forms complexes with this reagent. The recommended procedure involves the addition of sufficient EDTA to form the gallium complex and to provide a slight excess. The amount in excess is then determined by titration with

a standard ferric iron solution, with potassium benzohydroxamate as the indicator. It is impossible to detect the end-point visually because of the yellow colour of the uranyl ions, but this difficulty is readily overcome by employing the photometric method of end-point detection.

Although there is a negligible amount of information in the literature on the determination of trace amounts of gallium in non-ferrous materials, the absorptiometric method in which rhodamine B is used should be applicable after the preliminary extraction of the gallium from chloride solutions with diethyl ether.<sup>93</sup> By carrying out the solvent extraction in the presence of titanous chloride, the gallium is separated from most other elements, and the few that are co-extracted (*e.g.*, germanium and tin) do not react with the rhodamine B. After the ether extractions, the extracts are combined and the ether is removed by evaporation. The gallium is then dissolved in 6 M hydrochloric acid, and it is extracted from this medium into benzene as rhodamine-B chlorogallate. The determination is completed by measuring the absorbancy of the benzene extract.

### INDIUM

A preliminary separation is necessary for the determination of trace amounts of this element in non-ferrous materials and the extraction of the indium - 8-hydroxyquinoline complex with chloroform from sample solutions in the pH range 3.2 to 4.5 has so far been employed.<sup>94</sup> Although the indium - 8-hydroxyquinoline complex has a strong yellow colour in chloroform solutions, this is not suitable for the direct absorptiometric determination of indium because of the similar behaviour of many other elements, including Al, Ga, Bi, Cu and Sn<sup>II</sup>. For the determination of traces of indium in beryllium salts, the author<sup>95</sup> used the polarographic method to determine the indium content after the extraction of its 8-hydroxyquinoline complex. In this procedure the organic extracts are combined together and chloroform is removed by distillation. Then organic matter is destroyed by wet oxidation, and heat is applied to drive off the sulphuric acid completely. The residue is dissolved in hydrochloric acid, and iron and molybdenum, if present, are removed by extraction with diethyl ether. The indium content of the aqueous solution is finally determined by conventional polarography by using the well defined step for indium from a chloride base solution. If a square-wave polarograph is available for this determination, it should be possible to leave out the extractions with diethyl ether. Ferrett and Milner<sup>97</sup> also found this polarograph suitable for the determination of traces of indium in pure tin metal, after the preliminary removal of the major constituent as its volatile bromide. Cadmium unfortunately gives a peak almost coincident with the indium peak in a chloride base solution and the chemical separation of these elements is necessary in the analysis of samples containing both constituents. The cathode-ray polarograph is more suitable for the simultaneous determination of these two elements because of the slightly improved separation obtained with this instrument.<sup>65</sup>

The determination of alloying amounts of indium in non-ferrous materials is not likely to be a very frequent requirement and, moreover, recent developments in the analytical chemistry of this element indicate that such determinations should not present any serious difficulties. For instance, Irving and Rossotti<sup>96</sup> recently effected the separation of indium from many elements by extracting its iodide complex with diethyl ether. For alloy analysis the most convenient solution conditions are produced by making a sulphuric acid (1.5 N) solution of the sample 1.5 M in potassium iodide before carrying out the extraction process. This procedure separates indium from many elements, including gallium, beryllium and ferrous iron. Bismuth, copper, zinc, mercury and antimony are partly extracted with the indium, whereas cadmium and stannous tin are completely extracted. Volumetric methods are available for the determination of milligram amounts of this element. One suitable method involves the titration of the indium (2 to 80 mg) with a standard ferrocyanide solution, the amperometric method being used for detecting the end-point.<sup>97</sup> This titration is best carried out in a 0.1 M potassium chloride base solution at an applied potential of -0.75 volt against the S.C.E. Other methods are based on the very strong complex formed by indium with EDTA ( $\log K = 26$ ). Flaschka and Amin<sup>98</sup> succeeded in titrating indium directly in ammoniacal solutions containing tartrate ions by using Eriochrome black T as the indicator. If mercury, copper, cadmium, zinc, cobalt or nickel are also present in the sample solution, they can be readily masked as their cyanide complexes. It is possible to titrate the indium

with EDTA in solutions of pH 5 when morin is employed as the indicator.<sup>99</sup> This indicator causes the indium to fluoresce in ultra-violet light, and the procedure, therefore, consists in adding the EDTA solution until the fluorescence just disappears.

### IRON

Absorptiometric methods are suitable for the determination of this element when present in small alloying amounts in non-ferrous alloys. Many methods are based on the coloured complex formed by ferric ions with thiocyanate ions. Unfortunately, this complex is susceptible to variations in acidity, thiocyanate reagent concentration and temperature, but when these factors are controlled good results are obtained. Methods are available for the determination of iron in aluminium-base<sup>22</sup> and magnesium-base alloys,<sup>45</sup> beryllium salts<sup>100</sup> and copper-base alloys after the removal of copper as its insoluble oxalate.<sup>101</sup> These thiocyanate methods are not very convenient for routine control analysis, because of the necessity for strict controls, and in recent years methods in which use is made of the ferrous - *o*-phenanthroline complex have proved more satisfactory. This complex is free from the use of strict controls, since it is unaffected by wide variations in reagent concentrations, exposure to light and to normal changes in temperature. Such methods are so far available for the analysis of aluminium-base alloys,<sup>102</sup> pure tin<sup>21</sup> and tantalum metal.<sup>85</sup> Ferric ions also form coloured complexes suitable for the absorptiometric determination of this element with several other reagents, including thioglycollic acid and 2: 2'-dipyridyl.<sup>19</sup>

Although well defined steps are obtained for ferric ions from a variety of base electrolytes, there are few instances in non-ferrous analysis where the polarographic method is as useful as alternative methods. With copper-base alloys, it is necessary to remove the major constituent in the absorptiometric method. The same separation is also needed in polarographic analysis and a method proposed by Meites<sup>103</sup> involves the removal of the copper by reducing it to the metallic state through shaking a hydrochloric acid solution of the sample with amalgamated zinc. Iron and tin remain in the filtrate in their reduced states. After oxidation of the solution with potassium permanganate, the iron step is recorded from a citrate base solution of pH 5. A citrate base electrolyte is also used in a direct method for the determination of iron in zinc-base alloys.<sup>64</sup> For the analysis of tin - antimony - lead solders,<sup>47</sup> EDTA is included in a citrate base of pH 5. Under these conditions ferric ions produce a step before those for copper and bismuth, and this step is suitable for the determination of the iron in this type of material. In a method for iron in nickel-base alloys, a preliminary separation of the iron is carried out by precipitating it with ammonium hydroxide.<sup>104</sup> After filtration, the precipitate is dissolved in hydrochloric acid and the iron step is recorded from a base electrolyte consisting of 0.3 M triethanolamine, 1.0 M ammonium hydroxide and 0.85 M ammonium chloride.

Volumetric methods are satisfactory for the determination of iron in alloys when it is present as a major alloying constituent. The usual method involves the reduction of the iron in hydrochloric acid solution with stannous chloride, followed by titration with standard potassium dichromate after removal of the excess of the reductant by the addition of mercuric chloride. Before this type of procedure can be applied, however, the preliminary separation of the iron from other alloying constituents is frequently necessary. For example, in the analysis of nickel - cobalt - iron alloys, Chirnside, Cluley and Proffitt<sup>51</sup> separated the iron from the other constituents by the classical basic-acetate precipitation method. After filtration, the precipitate is dissolved in hydrochloric acid and the reduction with stannous chloride is applied. The selective separation of iron in metallurgical analysis is now, however, preferably achieved by solvent extraction, and these methods are considered in an excellent review by West.<sup>105</sup> Another volumetric method for iron employs titanous chloride as the titrant; this is added directly to ferric iron in sulphuric or hydrochloric acid solution until the red colour formed by iron with thiocyanate is just discharged. This method is more useful when many samples are received for analysis, because of the precautions necessary for the storage of titanous chloride solutions.

### LEAD

Trace amounts of this element in alloys can be readily determined by a method based on the extraction of the lead from other constituents with dithizone. The lead is extracted from strongly ammoniacal cyanide - citrate solutions, under which conditions the excess of

the dithizone reagent passes into the aqueous layer, leaving the lead dithizonate in the chloroform layer. The lead content is finally determined from the measurement of the absorbancy of the chloroform layer. Milner and Townend<sup>106</sup> used this method for the determination of traces of lead in brasses, bronzes, zinc-base alloys and tin-base white metals, and Coppins and Price<sup>21</sup> extended it to the analysis of pure tin.

Polarographic methods are the most suitable for small amounts of lead in alloys. After the separation of tin as metastannic acid in the analysis of copper-base alloys, the copper is complexed with cyanide ions and the lead step is recorded from an alkaline cyanide base electrolyte.<sup>107,108</sup> This method is direct and very much quicker than the usual gravimetric method. For lead in aluminium alloys the step from a hydrochloric acid base electrolyte is used.<sup>109</sup> Under these conditions ferric iron and copper give steps that precede the lead step and often cause difficulty in alloy analysis. In the recommended method, therefore, any ferric iron is reduced to the ferrous state and copper is removed from solution as the insoluble cuprous thiocyanate. A slightly modified form of this method is applicable to magnesium alloys.<sup>110</sup> A chloride base electrolyte is also suitable for lead in zinc-base Mazak alloys.<sup>64</sup> This determination is direct, and it is more useful than the dithizone method for the complete analysis of samples, since copper, cadmium and tin can be determined simultaneously. Similarly, copper and cadmium can be determined at the same time as lead in the analysis of tin metal and tin-base white metal.<sup>67</sup> The preliminary removal of the tin as its volatile bromide is necessary, and a square-wave polarograph is most suitable for white metals, since the copper content of these alloys is invariably greater than the lead. With a chloride base electrolyte, well separated peaks are obtained for copper, lead and cadmium. A chloride base solution is recommended for traces of lead in cobalt metal and salts<sup>111</sup> and in cadmium metal by conventional polarography.<sup>46</sup>

For the determination of large alloying amounts of lead, it is usually necessary to separate the lead from other constituents as its insoluble sulphate. The lead sulphate can be collected on a weighed sintered-glass crucible and then dried to constant weight after suitable washing. An alternative method involves re-solution of the lead sulphate precipitate in ammonium acetate, followed by titration of the lead with ammonium molybdate, with a 0.5 per cent. solution of tannic acid as the external indicator.<sup>38</sup> The titration of lead is now, however, more suitably carried out with EDTA, since an internal indicator can be used.<sup>112</sup> The lead sulphate precipitate is first dissolved in an ammonium hydroxide - ammonium chloride buffer solution of pH 10 containing Rochelle salt. Then a small quantity of a 0.2 per cent. solution of Eriochrome black T in triethanolamine is added and the titration with EDTA is carried out until the indicator colour changes from red to blue. In certain special alloys the prior separation of the lead may not be necessary, because the EDTA titration can be carried out in the presence of Hg, Zn, Cd, Cu, Co and Ni when these are complexed with cyanide.

#### MAGNESIUM

Absorptiometric methods are available for the determination of small amounts of this element, and those based on the red lake formed with titan yellow in the pH range 12 to 13 have been in use for many years. More recently, however, Solochrome cyanine has been advocated, since apparently this reagent is less susceptible to interference from impurities.<sup>113</sup> Its lake with magnesium is formed in solutions of pH 11, and in order to obtain such solution conditions, it is necessary to precipitate the magnesium from solution as its hydroxide. After filtration, the precipitate is dissolved in a measured amount of standard sulphuric acid and then the requisite amount of ammonium hydroxide is added to give the desired pH value. The use of this reagent in alloy analysis is not very convenient, therefore, unless a preliminary separation of the magnesium as its insoluble hydroxide is needed. Challis and Wood<sup>114</sup> confirmed this in an investigation of methods for the determination of magnesium in titanium-base materials. With alloys containing aluminium, manganese and chromium as alloying constituents, it proved necessary to carry out separations with cupferron and chloroform, zinc oxide and potassium permanganate, and finally the magnesium was recovered by precipitating it as the hydroxide. After this separation procedure, the Solochrome cyanine method is applicable and is preferred by these workers. For traces of magnesium in titanium sponge, however, the titan yellow method is more suitable, because fewer chemical separations are needed. After the removal of titanium by cupferron - chloroform extractions, organic matter in the aqueous layer is destroyed by wet oxidation and the titan yellow colour is then formed directly in a portion of this solution.

Aluminium alloys can contain up to 12 per cent. of magnesium, which is preferably determined volumetrically. A well established method involves the precipitation of the magnesium with 8-hydroxyquinoline, followed by the usual bromimetric titration procedure.<sup>22</sup> It is necessary, however, to carry out a preliminary separation of the magnesium, and the usual method involves the solution of the sample in sodium hydroxide, which separates the magnesium, copper, nickel, iron and manganese as an insoluble residue. This residue is dissolved in nitric acid and, after the separation of iron, manganese and residual aluminium, cyanide is added to the solution to complex copper and nickel, and the magnesium is precipitated with 8-hydroxyquinoline. Another volumetric method for magnesium involves direct titration with EDTA, with Eriochrome black T as the indicator.<sup>115</sup> Although heavy metals such as copper and nickel do not interfere when complexed with cyanide, the magnesium must be separated from other alkaline earths. This titration is applicable to aluminium alloys after the separation of the magnesium by a procedure similar to that used in the 8-hydroxyquinoline method. This method can only be considered, therefore, as an alternative to the 8-hydroxyquinoline method.

#### MANGANESE

Minor alloying amounts of this element are determined by absorptiometric procedures, whereas major amounts are best determined volumetrically. The absorptiometric procedures are based on the oxidation of the manganese to permanganate, which is conveniently effected by boiling a sulphuric - phosphoric acid solution of the sample with potassium periodate. Interference from other alloy constituents is readily eliminated by adopting the procedure of taking absorbancy measurements after the oxidation process and also after the selective reduction of the permanganate with sodium nitrite. Absorptiometric methods are recommended for the determination of the manganese content of aluminium alloys,<sup>22</sup> magnesium alloys,<sup>45</sup> beryllium salts<sup>71</sup> and copper-base alloys.<sup>116</sup> A polarographic method is proposed by Spalenka<sup>117</sup> for manganese in aluminium alloys. It is based on the step from an alkaline cyanide base solution containing metol to prevent air-oxidation of the manganese. However, polarographic methods are never likely to be able to compete with the simplicity and directness of absorptiometric methods.

A well established volumetric method consists in the oxidation of manganese in nitric acid solution to the permanganate state with sodium bismuthate. After the removal of the excess of bismuthate by filtration through ignited asbestos, a standard ferrous ammonium sulphate solution is added to give an excess and the amount of this reagent in excess is then determined by titration with a standard potassium permanganate solution until a faint pink colour is produced. For accurate results the solutions must be free from every trace of chloride ions and nitrous acid must also be absent. Chromium, cobalt and vanadium also cause interference in this determination. Gibson<sup>118</sup> used this procedure for the analysis of uranium - manganese alloys containing from 1 per cent. to greater than 90 per cent. of the second constituent. The error in the manganese determination did not exceed  $\pm 0.25$  per cent. A more recent volumetric method is free from the interferences of the bismuthate method. It is based on the titration of manganous ions in a pyrophosphate solution of pH 6 to 7 with a standard permanganate solution, the large break in potential at the endpoint being used to detect the completion of the titration.<sup>119</sup> This titration is direct and the need for filtration so necessary with the bismuthate method is obviated. It is suitable for the determination of amounts of manganese varying from a few milligrams to 200 mg, and the accuracy of the titration appears to be limited only by the accuracy of the volumetric measurements. There is no interference from large amounts of chloride, nitrate, sulphate, iron<sup>III</sup>, cobalt<sup>II</sup>, copper, nickel, chromium<sup>III</sup>, molybdenum<sup>VI</sup>, tungsten<sup>VI</sup>, uranium<sup>VI</sup>, zinc, aluminium, magnesium and cadmium, the non-interference of chloride, cobalt and chromium representing an important improvement over the previous method. Large amounts of vanadium cause difficulties, but this interference can be overcome by carrying out the titration at the lower pH value of 3 to 3.5.

#### MOLYBDENUM

Absorptiometric methods are available for the determination of a wide range of molybdenum contents in non-ferrous alloys. The coloured complex formed by molybdenum with thiocyanate ions is very suitable for absorptiometric work and the following solution conditions

are recommended for the formation of this complex: 3·8 N sulphuric acid, 0·15 M ammonium thiocyanate, 0·20 M perchloric acid, 0·05 M stannous chloride and 0·02 M iron. Davis<sup>120</sup> employed this complex in a method for the determination of the molybdenum content of alloys of the nickel-base Permalloy type, absorbancy readings being taken at a wavelength of 460 m $\mu$ . More recently it has been used in conjunction with the differential system of measurement for the determination of from 5 to 30 per cent. of molybdenum in uranium-base ternary alloys of the type uranium - molybdenum - niobium.<sup>121</sup> In this work it proved necessary to take absorbancy readings at a wavelength of 500 m $\mu$  so as to avoid the interference occurring at 460 m $\mu$  from uranyl ions. In the absence of niobium the complex formed by molybdenum with hydrogen peroxide is suitable for absorptiometric work and it has been used for the determination of up to 20 per cent. of molybdenum in its binary alloys with uranium by employing the differential technique.<sup>122</sup> This determination is best carried out in solutions approximately 1·5 M in sulphuric acid and 0·18 M in hydrogen peroxide, and when absorbancy measurements are taken at a wavelength in the range 360 to 380 m $\mu$  it is possible to correct for the small absorbancy from uranyl ions.

Molybdenum gives well defined steps in a variety of base electrolytes, and Wolfson<sup>104</sup> used the steps from a 0·75 N sulphuric acid - 0·5 M citric acid base solution for the direct determination of this constituent in nickel-base alloys. Molybdenum gives two steps from this base solution with half-wave potential values of -0·35 volt and -0·85 volt, respectively. Copper and iron in the sample produce steps that interfere with the first molybdenum step, but the second step is free from interference and is suitable for this determination, after the use of additional condensers to decrease the large oscillations in the step. Because of this need for extra damping, the absorptiometric method appears more attractive for routine analysis. However, a polarographic method is suggested for the determination of amounts of molybdenum up to 5 per cent. in titanium-base alloys.<sup>123</sup> The separation of the molybdenum is necessary, and this is achieved by extracting it into ether from a solution of the sample, 4·7 N in hydrochloric acid and 3·6 N in sulphuric acid. After the evaporation of the ether from the combined extracts, the polarogram is recorded from a perchloric acid base solution and the molybdenum content is evaluated from the step with a half-wave potential of -0·235 volt against the S.C.E.

### NICKEL

Direct absorptiometric methods are suitable for the determination of small alloying amounts of this element. They are based on the red coloured complex formed with dimethylglyoxime in ammoniacal solution, and much information is available on the best conditions for the formation of a stable complex. Direct methods are recommended for the determination of nickel in aluminium alloys,<sup>22</sup> magnesium alloys,<sup>84</sup> uranium metal,<sup>124</sup> beryllium salts<sup>77</sup> and pure metallic tin.<sup>21</sup> For the analysis of copper-base alloys, however, a less direct method is used, because of the need for removing the major constituent. Various methods for removing copper have been reported, including electrolysis and deposition on aluminium foil, but the author<sup>116</sup> found the most expedient method to consist in precipitating the bulk of the copper with potassium iodide, followed by the formation of the nickel - dimethylglyoxime complex directly in the filtrate. The correction for the absorbancy of the small amounts of unprecipitated copper is readily obtained by taking absorbancy readings after the decomposition of the nickel complex with hydrogen peroxide.

Polarographic methods are more direct than the absorptiometric method for the analysis of certain types of copper-base alloys. For example, by using the nickel step from an alkaline cyanide base solution it is possible to determine the nickel content of cupro-nickels and aluminium bronzes by conventional polarography.<sup>125</sup> With alloys containing zinc, however, it is necessary to separate this constituent before recording the nickel step. This difficulty does not occur with tin-bronze samples on using a 0·2 M ammonium chloride - M ammonium hydroxide base solution in conjunction with the square-wave polarograph.<sup>126</sup> Moreover, it is possible to determine the zinc content simultaneously with the nickel content. Tin is the only constituent to prove troublesome, because of its insolubility in the alkaline base electrolyte, but this element is readily removed as its volatile bromide in the initial solution of the sample. The square-wave polarograph is also applicable to the direct determination of nickel in aluminium alloys by using the peak from a 0·03 M potassium cyanide - M potassium hydroxide base solution containing sodium sulphite to suppress the air oxidation of the

manganese cyanide complex to manganese dioxide.<sup>67</sup> This method is direct and is applicable to a few milligrams only of sample, but it possesses no important advantages over the absorptiometric method. The polarographic method is extremely useful for the determination of small amounts of nickel impurity in cobalt metal and salts.<sup>111</sup> The polarogram is recorded from a pyridine base solution, under which conditions the nickel step is well separated from the cobalt step.

Volumetric methods are suitable for the determination of larger alloying amounts of this constituent and one outstanding method involves the addition of a slight excess of a standardised potassium cyanide solution to complex the nickel, followed by titration with silver nitrate back to the potassium iodide end-point.<sup>127</sup> Nickel can also be titrated with EDTA, but there is so much interference in this titration from other elements that it is usually only applicable after the separation of the nickel from other constituents.<sup>112</sup> Flaschka,<sup>128</sup> for example, has used this titration after the separation of the nickel with dimethylglyoxime. The use of EDTA is more important, however, in such analytical problems as the determination of nickel in the presence of small amounts of cobalt.<sup>129</sup> In a suggested method for this determination sufficient EDTA is added to complex the nickel and cobalt and leave a slight excess. This excess is titrated with magnesium sulphate back to the colour change of the Eriochrome black T indicator. Then 2 to 3 ml of hydrogen peroxide are added to the solution, followed by 1 g of potassium cyanide. Under these conditions the cobalt complex is quite stable, so that the cyanide ions cause the liberation of the amount of EDTA equivalent to the nickel only. After the solution has been allowed to stand for about 5 minutes, the amount of liberated EDTA is determined by titration with magnesium sulphate to the production of the original colour of the indicator.

#### NIOBIUM AND TANTALUM

Microgram amounts of niobium can be determined absorptiometrically by using its coloured thiocyanate complex. In one of the published procedures, the complex is formed directly in the aqueous sample solution and absorbancy measurements are made on this solution.<sup>130</sup> In the other procedure the complex is extracted into an organic solvent for absorbancy measurements.<sup>131</sup> The reported conditions for the formation of the niobium thiocyanate are, however, so critically dependent on such facts as the thiocyanate concentration, acidity and temperature that great care is needed in using this complex in analysis. From the results of a recent study, however, more suitable solution conditions have been developed for the formation of the niobium complex.<sup>132</sup> In a method for the analysis of tantalum metal for traces of niobium (0·01 to 0·3 per cent.), the niobium - thiocyanate complex is extracted into ether for taking the absorbancy readings.<sup>133</sup> For the determination of niobium in its binary alloys with titanium,<sup>134</sup> a separation of the niobium is effected by precipitating it with tannic acid from a boric acid - hydrofluoric acid solution of the sample. After two further tannic acid precipitations, the niobium content is determined by the direct thiocyanate method. However, from the results of recent work on the solvent extraction of niobium, the application of this technique should greatly improve this particular separation.<sup>135</sup> Another absorptiometric method for niobium is based on the yellow colour produced by the addition of hydrogen peroxide to a strong sulphuric acid solution of the sample.<sup>136</sup> This is not a very strongly coloured complex and the concentrated acid solutions need careful handling during the measurement of absorbancies. Even so, this complex has proved useful for the determination of small alloying amounts of niobium in uranium-base materials.<sup>137</sup> In methods for the analysis of uranium - zirconium - niobium and uranium - tin - niobium alloys, the niobium - peroxy complex is formed in a freshly fumed sulphuric acid solution of the alloy by the addition of a sulphuric acid - hydrogen peroxide mixture, and absorbancy readings are taken at a wavelength of 362 m $\mu$ . The main advantage of these methods is that chemical separation of the niobium is avoided.

Tantalum forms with pyrogallol a coloured complex that can be used for the determination of small amounts of this element.<sup>138</sup> Unfortunately, however, several elements cause interference in this determination, which is really only useful after the separation of the tantalum with the niobium from other constituents of the sample by cellulose chromatography.<sup>139</sup> Small amounts of tantalum are more suitably determined by radioactivation analysis,<sup>140</sup> the neutron irradiation of the sample forming tantalum-182, which is a  $\gamma$ -emitter and has a half-life of 111·2 days. When the sample is allowed to stand after irradiation, the

activities from many other constituents die away and by this means it is possible to determine tantalum in the presence of Nb, Fe, Mn, Ti, Sn, Zr and Si without chemical separation. The count obtained from an irradiated sample can be made more specific for the tantalum-182 isotope by the use of a sodium iodide crystal spectrometer and a single-channel kick sorter operating in a narrow channel centred on the tantalum-182 photopeak at 1.1 MeV.<sup>141</sup>

The methods for the determination of greater alloying amounts of niobium or tantalum involve the preliminary separation of these elements from other sample constituents. This separation is now most suitably accomplished by extraction with *isobutyl methyl ketone* from a fluoride solution of the sample that is 10 M in hydrofluoric acid, 6 M in sulphuric acid and 2.2 M in ammonium fluoride.<sup>135</sup> The earth-acid element is then extracted from the combined *isobutyl methyl ketone* layers with aqueous hydrogen peroxide, which is evaporated to fumes of sulphuric acid to remove the hydrogen peroxide and any hydrofluoric acid. On cooling, this solution is diluted with hydrochloric acid containing ammonium oxalate and the niobium or tantalum is recovered by precipitation with tannic acid after adjusting the pH to 4.5. The precipitate is recovered by filtration and is ignited to niobium pentoxide or tantalum pentoxide, which is finally weighed. In some samples, however, both elements are present and the final residue is a mixture of niobium and tantalum pentoxides. The procedure then to be employed for determining each element depends upon the relative amounts of the constituents. Usually it is necessary to separate them by cellulose chromatography<sup>6</sup> and to complete their determination gravimetrically as before. However, when the tantalum content is low, it may be more advantageous to use activation analysis. Similarly, absorptiometry may be more suitable in samples with low niobium contents.

### SILICON

Silicon is present in many non-ferrous materials either as a minor alloying constituent or as a trace impurity, and the determination of the amount of this element is now invariably achieved by an absorptiometric procedure. This method is based on the formation of yellow silicomolybdate complex ions, which can be produced in mineral acid solutions under suitable acidity conditions. When a 5-minute period is allowed for the development of the yellow colour in solutions containing 5 g of ammonium molybdate per litre, the optimum acidity for the full formation of this complex is in the range from 0.05 to 0.16 N.<sup>142</sup> This coloured complex is eminently suitable for the routine determination of the silicon content of any type of aluminium alloy containing up to about 8 per cent. of this constituent.<sup>22</sup> The method simply consists in dissolving the sample in sodium hydroxide solution contained in a covered stainless-steel beaker. Then the lid and walls are washed with water and a measured amount of a standard nitric acid solution is added to the beaker while its contents are being stirred. On cooling, this solution is in the correct acidity range and the silicomolybdate ions are formed on the addition of an ammonium molybdate solution. The silicon content of the sample is finally determined by measuring the absorbancy of the solution after a standing period of at least 5 minutes.

The silicomolybdate colour is unfortunately too insensitive for the determination of small amounts of silicon in non-ferrous materials. Greater sensitivity can be obtained in this procedure, however, by reducing the silicomolybdate ions to molybdenum blue. Stannous chloride is the most sensitive reducing agent for the production of molybdenum blue, but other reagents have been used for this reduction, including ferrous sulphate in the presence of oxalate,<sup>143</sup> ascorbic acid,<sup>144</sup> hydrazine,<sup>145</sup> hydroxylamine<sup>146</sup> and hydroquinone.<sup>147</sup> The reduction procedure cannot be applied to silicomolybdate ions in nitric acid solutions and the usual method makes use of controlled acidity to prevent possible interference from the reduction of phosphomolybdate, vanadomolybdate and arsenomolybdate ions. It is necessary to add sulphuric acid, after the formation of the silicomolybdate ions, to make the solution 2 to 6 N in this acid before the reduction with stannous chloride is carried out. Further details of this procedure are included in the following method for the determination of the silicon content of magnesium alloys containing less than 0.35 per cent. of silicon<sup>84</sup>: dissolve 0.5 g of sample in 7.5 ml of 10 N sulphuric acid and 40 ml of water. Boil, oxidise with a few drops of bromine and then boil off any excess of this reagent. Cool and dilute the solution to 100 ml with water. To a 10-ml aliquot of this solution, add 15 ml of water and then 5 ml of 5 per cent. ammonium molybdate reagent and allow the solution to stand for 5 minutes. Then add 10 ml of 10 N sulphuric acid followed by 5 ml of 0.25 per cent. stannous chloride

and dilute to a volume of 50 ml. Measure the absorbancy of this solution, using Ilford No. 606 filters with a Spekker absorptiometer. Before referring this reading to a calibration graph to obtain the silicon content of the sample, correct it for the absorbancy obtained in a reagent-blank determination.

Other applications of the molybdenum-blue complex include the determination of 1·5 to 100 p.p.m. of silicon in beryllium oxide and various salts of beryllium, including the sulphate, hydroxide and ammonium oxalate.<sup>148</sup> For the determination of 0·001 to 0·35 per cent. of silicon in calcium metal,<sup>149</sup> a combination of a sodium hydroxide attack followed by solution of the resulting sludge in hydrochloric acid is employed to attain complete solution of the sample. A similar method is also used for the analysis of aluminium samples containing from 0·01 to 0·5 per cent. of silicon.<sup>150</sup> In a procedure for bismuth metal,<sup>151</sup> the major constituent is removed as its volatile bromide and the remaining residue is examined for silicon. This residue is fused with sodium carbonate and, after extraction of the cooled melt with water, the molybdenum-blue complex is formed in the resulting solution. This method is claimed to be suitable for the determination of 2 to 125 p.p.m. of silicon in bismuth. In a subsequent method for the analysis of bismuth oxide,<sup>144</sup> the molybdenum-blue complex is formed in the presence of the bismuth after reduction of the silicomolybdate ions with ascorbic acid. The initial solution of the sample is produced by fusing it with sodium carbonate and by dissolving the cooled melt in a measured volume of 5*N* hydrochloric acid. This method is suitable for the determination of 5 to 35 p.p.m. of silicon with an error of less than 1·5 p.p.m. of silicon.

#### SILVER

Several procedures are available for the determination of alloying amounts of this element. Gravimetric methods are based on the insoluble silver halides. The silver chloride precipitate is generally preferred, because it is less sensitive to light than the other silver halides. After the precipitation of silver chloride, the solution is allowed to stand in the dark to permit the coagulation of the precipitate. Then the determination is completed by filtration through a sintered-glass crucible, followed by weighing the silver chloride precipitate. This is an accurate method that can be used for the determination of the silver content of silver solders.<sup>152</sup> Controlled-potential electrolysis methods are also available for the analysis of silver solders. Diehl and Butler<sup>153</sup> deposited the silver from an ammoniacal solution of the alloy with oxygen passing through the solution. After the silver determination the copper content of the alloy can also be obtained by electro-deposition. The sample solution is acidified by the addition of nitric acid, hydroxylamine sulphate is added as an anode depolariser and then the deposition of the copper is carried out. In a procedure recommended by Broadbank and Winram,<sup>154</sup> the silver is separated from other alloying constituents by electrolysing a perchloric acid solution of the sample.

A useful volumetric method for silver is based on ammonium thiocyanate as the titrant. The end-point of the titration is detected by including ferric iron in the solution so that the red coloration of ferric thiocyanate is produced after the completion of the titration. This titration procedure has been used for the determination of the silver content of silver-zirconium<sup>155</sup> alloys and of white-metal samples.<sup>38</sup> Another volumetric procedure which may be useful in metallurgical analysis has been proposed by Cheng.<sup>156</sup> It is based on the precipitation of the silver from an ammoniacal solution of the sample with 1:2:3-benzotriazole. Ethylenediaminetetra-acetic acid is included in the solution to prevent interference from several other elements. After filtration of the solution, the precipitate is dissolved in a small quantity of diluted nitric acid (1 + 1) and the resulting solution is neutralised with ammonium hydroxide. Then sufficient of a 0·05 *M* cyanide solution is added to form the silver complex and to provide an excess. The excess of cyanide is determined by titration with a standard silver nitrate solution, with potassium iodide as the indicator.

Absorptiometric methods are suitable for the determination of trace amounts of silver. One method is based on the red-violet coloration given by *p*-dimethylaminobenzylidenerhodanine in acid solutions (0·05 *N*).<sup>19</sup> A fine dispersion of the silver-rhodanine precipitate is formed for amounts of silver in the range 1 to 2  $\mu\text{g}$ , and fortunately this dispersion is fairly stable. This procedure is used for the determination of traces of silver in pure tin metal.<sup>19</sup> The rhodanine reagent has also been employed by Ringbom<sup>157</sup> in an indirect method for silver. The silver is precipitated as its rhodanine complex from a dilute sulphuric acid solution of the sample and, after filtration, the precipitate is washed with ethanol to remove excess of

the precipitant from it. The precipitate is then dissolved in alkaline potassium cyanide and absorbancy measurements are taken for the resulting yellow solution. Ringbom used this method for the determination of trace amounts of silver in electrolytic copper.

### THORIUM

Low alloying amounts of this element can be determined absorptiometrically by using the coloured complex produced with disodium 1-(o-aronphenylazo)-2-naphthol-3:6-disulphonate,<sup>158</sup> better known as thoronol. When this complex is formed in solutions of pH 1, it is very stable for a period of several hours, and Mayer and Bradshaw<sup>159</sup> have used it for the determination of thorium in magnesium alloys. In the recommended method the thorium is first separated from magnesium by precipitation with ammonium hydroxide, and then it is removed from zirconium by precipitating it along with the rare earths as their insoluble oxalates. This latter separation is necessary because zirconium also forms a coloured complex with thoronol. After filtration, the oxalates are converted to perchlorates and the absorptiometric determination of the thorium is completed in the presence of the rare earths. There is sufficient evidence available now, however, to show that the precipitation of thorium as its oxalate is not perfectly quantitative,<sup>160</sup> although in the analysis of the magnesium alloys the rare-earth oxalate precipitate probably helped to carry down the last traces of thorium. In view of this behaviour a separation process used in mineral analysis may be more reliable in alloy analysis, especially with samples containing thorium in the absence of rare earths.<sup>161</sup> The thorium is precipitated as its insoluble fluoride in the presence of lanthanum fluoride as carrier and, after filtration, the precipitate is dissolved in aluminium nitrate solution. The thorium is separated from this solution by extraction into mesityl oxide. It is then stripped from the combined organic layers with water and the thoronol complex is formed directly in this solution after its pH has been adjusted to 1 with perchloric acid.

Volumetric methods are now replacing the gravimetric methods for the determination of milligram amounts of thorium, and one such method employing EDTA as the titrant is proving very useful in alloy analysis. Fritz and Ford<sup>162</sup> first titrated thorium with EDTA, using alizarin red S as the indicator. This indicator forms a red lake with thorium at pH 2.8, and the procedure consists in titrating with EDTA until the red lake is discharged. Other indicators are now available for this titration and they include pyrocatechol violet<sup>163</sup> and thoronol.<sup>164</sup> Since thorium forms its complex with EDTA at fairly low pH values, it is often possible to apply the titration without any chemical separation of the thorium. Thus Furby<sup>165</sup> determined the thorium content of thorium - uranium alloys containing less than 60 per cent. of uranium by direct titration, using the alizarin red S indicator. For alloys with more than 60 per cent. of uranium, however, preliminary separation proved necessary, and the recommended procedure involves the precipitation of thorium as its benzoate complex in the pH range 1.5 to 2.5, re-solution of the precipitate in hydrochloric acid after filtration, and then titration with EDTA. The best titration procedure under these conditions consists in adding sufficient EDTA to complex the thorium and leave a slight excess, followed by titrating this excess with a standard iron solution, with salicylic acid as the indicator. Similarly, Milner and Sneddon<sup>166</sup> determined the thorium content of thorium - cerium alloys without any chemical separations, the titrations being carried out on a perchloric acid solution of the sample adjusted to pH 2.2. At this pH  $Ce^{3+}$  ions are not complexed with EDTA, and the method consists in adding an excess of EDTA to complex the thorium, followed by the titration of this excess of reagent with a standard thorium perchlorate solution, with Eriochrome cyanine as the indicator. In a recent method for the determination of thorium in its binary alloys with tungsten,<sup>167</sup> an excess of EDTA is added to complex the thorium and the amount in excess is determined by titration with a standard thorium solution, with alizarin red S as indicator. Interference from tungsten in this determination is prevented by the inclusion of hydrogen peroxide in the sample solution.

When it is necessary to effect the separation of the thorium from other alloy constituents before applying the EDTA titration, the separation procedure based on the solvent extraction of thorium nitrate into mesityl oxide is very useful.<sup>168</sup> It is usual to saturate the sample solution with aluminium nitrate before extracting with the organic solvent, and it is then possible to separate the thorium from all other elements with the exception of uranium,

zirconium and vanadium. Of these elements uranium causes little difficulty, but zirconium forms a very stable complex with EDTA under the conditions for the titration of thorium. Milner and Woodhead<sup>169</sup> used this separation process in the analysis of thorium - aluminium alloys, calcium nitrate being used instead of aluminium nitrate, however, because of the need for determining the aluminium content of the alloys. In independent work on this alloy system, Banks and Edwards<sup>170</sup> saturated the sample solution with lithium nitrate. In cases when this solvent-extraction process is inapplicable, as for example in the analysis of alloys containing zirconium, it is possible to effect the separation of the thorium by precipitating its fluoride from 10 M hydrofluoric acid solutions. Milner and Barnett<sup>171</sup> found this procedure useful in the analysis of thorium - zirconium alloys and uranium - thorium - zirconium alloys. After the precipitate has been separated by the use of a centrifuge, it is washed and taken into solution by fuming with perchloric acid. Because of the difficulty of removing the last traces of fluoride by this procedure, the EDTA titration is best carried out in acetate-buffered solutions of pH 5 with boric acid present to form a complex with any fluoride ions. The thorium is made into a complex by the addition of a slight excess of EDTA, and the excess of this reagent is determined by titration with a standard iron solution, with salicylic acid as the indicator.

### TIN

The determination of alloying amounts of tin is required in the analysis of several types of non-ferrous alloys, and volumetric methods are most convenient after the reduction of the tin to the stannous state. With some alloys the titration procedure is applicable directly to the sample solution, whereas with others it is necessary to carry out a preliminary separation of the tin. In a direct method for the determination of the tin content of aluminium alloys,<sup>172</sup> most of the tin is in the stannous state after the solution of the sample in hydrochloric acid, and complete reduction is ensured by boiling the solution with antimony powder. After cooling the solution in the absence of air, potassium iodide is added and the tin is titrated by the addition of a standard potassium iodate solution from a semi-micro burette to the starch end-point. In a recommended method for copper-base alloys, the copper is first removed from solution by precipitation as its oxalate.<sup>172</sup> The tin is then reduced by boiling the acidified filtrate with metallic nickel in the form of a spiral, which can be easily removed from the solution before the titration with potassium iodate. Any antimony in the sample is plated on the nickel spiral during the reduction process. The nickel-reduction procedure is also directly applicable to the determination of the tin content of white metals on taking a 250-mg sample and dissolving it in hydrochloric acid with the help of hydrogen peroxide.<sup>173</sup> Then, after the addition of sodium chloride to the solution, the nickel-reduction procedure is carried out and the titration with potassium iodate completed as before. However, when the complete analysis of a white-metal sample is required, the dry-chlorine method of opening the analysis is worthy of consideration.<sup>174</sup> This technique separates the tin and the antimony from the other constituents of the sample and the tin content is finally determined by titration with a standard iodine solution after reduction with metallic antimony. In a method for tin in lead-sheathing alloys,<sup>31</sup> the sample is attacked with a mixture of acetic acid and hydrogen peroxide and finally with hydrochloric acid. The tin is reduced with hypophosphite before being titrated with standard iodine. When it is necessary to separate the tin from other alloying constituents before applying the titration procedure, sulphide precipitation is often used. In a method for the determination of 0·05 to 5 per cent. of tin in its binary alloys with titanium, Norwitz and Codell<sup>175</sup> first dissolved the sample in sulphuric acid and then oxidised the titanium with potassium permanganate. After the addition of tartaric acid to the sample solution, the precipitation of the tin is carried out by the passage of hydrogen sulphide. Then the sulphide precipitate is removed by filtration, dissolved in mineral acid and the tin content of the solution is determined volumetrically. Similarly, the separation of tin as its sulphide is used in the analysis of uranium ternary base alloys containing niobium and tin as alloying constituents.<sup>176</sup> This separation procedure is very time-consuming, however, since it is necessary to allow the sulphide precipitate to digest for 12 hours before filtration. The hypophosphite reduction of the tin is employed in the final volumetric process.

The determination of trace amounts of tin in non-ferrous materials is often achieved by polarographic methods by using the well defined step given by this element from a hydrochloric acid base solution. Unfortunately, this determination is not direct for samples

containing lead in addition, because this element gives a step coinciding with the tin step. The procedure adopted in such cases consists in the determination of tin plus lead from a hydrochloric acid base solution, followed by the determination of lead only from a more alkaline base electrolyte.<sup>59</sup> By this means the tin content is obtained by difference, and clearly this method is only applicable for suitable ratios of tin and lead. Nickelson and Randles successfully used this procedure for the determination of traces of tin in zinc-based Mazak alloys,<sup>64</sup> the lead content of these alloys being comparable with that of the tin.

An absorptiometric method for the determination of small amounts of tin has assumed importance in recent years; it is based on the complex formed by tin with dithiol. For satisfactory results with this method, however, it is necessary to include a suitable dispersing agent in the solution to disperse the tin - dithiol complex. On using Belloid TD, Kenyon and Ovenston<sup>176</sup> obtained stable conditions over a period of one to two hours for solutions containing up to 10 µg of tin per ml. With Teepol as the dispersing agent, Williams and Whitehead<sup>177</sup> were able to determine the tin content of solutions containing up to 16 µg of tin per ml. American workers<sup>178</sup> prefer to use the dispersing agent Santomerse S manufactured by the Monsanto Chemical Co. Unfortunately, a number of heavy metals also react with dithiol and the direct application of this method in analysis is often not possible without the preliminary separation of the tin. Distillation is very effective for this particular separation. Onishi and Sandell<sup>179</sup> first distil from hydrochloric acid solutions at 160° C to remove arsenic, antimony and germanium. Then hydrobromic and hydrochloric acids are added and the distillation at 160° C is continued to separate the tin. This type of procedure is suggested for the determination of the tin content of aluminium - silicon alloys,<sup>178</sup> sheet brass<sup>178</sup> and pure iron.<sup>179</sup>

#### TITANIUM

Absorptiometric methods are available for the determination of both large and small alloying amounts of this element, high-precision spectrophotometry being used for the former. These methods are based on the yellow colour produced when hydrogen peroxide is added to a nitric or sulphuric acid solution of titanium. The acid concentration is not critical, but the intensity of the colour produced in sulphuric acid solutions is slightly weaker than that produced in nitric acid solutions. Vanadium is the most serious interfering element in the titanium determination, but fortunately it is not a common constituent of non-ferrous alloys. The peroxide complex is used in a method for the determination of titanium in aluminium alloys, which usually do not contain any interfering elements.<sup>22</sup> It is generally necessary, however, to make a correction for the light absorption of coloured ions in the sample solution (for example, copper, nickel or iron), especially when they are present in large amounts. Other applications of this complex include the determination of titanium in tantalum metal<sup>65</sup> and refractory materials.<sup>180</sup> In the field of high-precision spectrophotometry, this complex is used for the determination of the titanium content of pure titanium metal,<sup>181</sup> titanium - oxygen alloys and titanium - uranium alloys.<sup>182</sup> Unfortunately, the peroxide complex is not sensitive enough for the determination of trace amounts of titanium in metals and alloys. The coloured complex given by titanium with disodium 1:2-dihydroxybenzene-3:5-disulphonate (tiron) is more sensitive and generally meets these requirements. It is used, for example, in a method for the determination of traces of titanium in cathode nickel tubing.<sup>183</sup> The titanium is separated from the nickel by precipitation with ammonium hydroxide, ferric hydroxide being used as a carrier, and, after the separation and re-solution of the precipitate, the titanium - tiron complex is formed. Before the absorbancy of the titanium complex is measured at a wavelength of 399 mµ, however, it is necessary to bleach the colour of the iron complex with sodium dithionite.

A well defined polarographic step is obtained for titanium from a base electrolyte consisting of 1.2 M ammonium sulphate, 0.5 M sulphuric acid and M tartaric acid. In applying this step to the determination of 0.06 to 3 per cent. of titanium in aluminium alloys, Graham and Hitchen<sup>184</sup> carried out a preliminary separation of the titanium from certain other constituents of the sample. This involved attacking the sample with sodium hydroxide and separating the insoluble part containing the titanium. After the titanium has been taken into solution by treating the insoluble matter with hot sulphuric acid, sufficient ammonium sulphate and tartaric acid is added to give the solution the composition of the base electrolyte. Then the titanium step is recorded and the determination completed in the usual way. Although

the separation procedure in this method is not troublesome, it makes the polarographic method less direct than the absorptiometric method for this determination. Graham, Hitchen and Maxwell<sup>185</sup> also used this step for the determination of the titanium content of nickel-base alloys, including Nimonic, Monel and Inconel types of alloy. In this method the titanium is separated from many other alloying constituents by applying mercury-cathode electrolysis to a sulphuric acid solution of the sample. Then the other constituents of the base electrolyte are added and the step is recorded. It is very doubtful whether the titanium peroxide method could be applied directly to these alloys, because of the strong natural colour of the nickel ions in solution and, in view of this, there should be little to choose between the polarographic method just described and a suitable absorptiometric method.

Volumetric methods are available as an alternative to the high-precision spectrophotometric method for the determination of large alloying amounts of titanium, and details of one suitable method are included in a procedure for the determination of the titanium content of titanium metal.<sup>186</sup> The sample is first fused with potassium bisulphate and, on cooling, the melt is extracted with diluted hydrochloric acid (1 + 1). This solution is boiled with a quantity of amalgamated zinc shot and finally passed down a column of amalgamated zinc in an atmosphere of carbon dioxide. The collected solution is immediately titrated with a standard ferric alum solution to the thiocyanate end-point. This type of procedure is not specific for titanium, because several elements, including chromium, molybdenum, tungsten and vanadium, are reduced in the Jones reductor. In titanium metal, the amounts of these potential interfering elements are very small and can be discounted, but if a separation of titanium is needed, then precipitation with sodium hydroxide is recommended.

### URANIUM

Minor alloying amounts of this element can be determined satisfactorily by absorptiometric methods. A useful method in acidic solutions makes use of the yellow colour formed by uranyl ions with thiocyanate ions in solutions of pH 1.5. The intensity of the colour produced, however, depends upon the concentration of thiocyanate ions, so that fairly strict controls must be applied in the preparation and in the addition of this reagent. Interference from ferric iron is prevented by reducing it with stannous chloride and under these conditions molybdenum is reported as the main interfering element. On applying this method to the determination of amounts of uranium up to about 5 per cent. in its binary alloys with bismuth, Milner and Edwards<sup>187</sup> encountered interference from a coloured complex formed by thiocyanate ions with bismuth ions. It proved possible to suppress the bismuth interference, however, by complexing the bismuth ions with EDTA before the addition of the thiocyanate reagent. The uranium-thiocyanate complex formed in an aqueous acetone mixture is recommended for the determination of small alloying amounts of this constituent in its binary alloys with aluminium and with thorium.<sup>187</sup> A direct method is used for the aluminium-base alloys, but with the thorium-base alloys the preliminary separation of the uranium by solvent extraction is necessary. Another absorptiometric method for uranium employs the colour formed with hydrogen peroxide in alkaline carbonate solutions.<sup>19</sup> In alloy analysis this coloured complex is generally only useful after the separation of the uranium from other constituents.

Polarographic methods are also available for the determination of small amounts of uranium. A suitable base solution for conventional polarography is 2*N* in sulphuric acid and 2*N* in hydroxylamine sulphate. Sensitivity is improved by using the square-wave polarograph with a sulphuric acid base solution.<sup>67</sup> However, Ferrett and Milner<sup>188</sup> obtained much better results with this instrument by using a *M* perchloric acid base solution. Uranium concentrations of the order of 0.1 µg per ml can be determined by this method by using the peak occurring at -0.3 volt against the mercury-pool anode. This base solution is very convenient in applied analysis, since the uranium can be dissolved in nitric acid and this solution then evaporated to fumes of perchloric acid. Still smaller amounts of uranium can be determined by a fluorimetric method, which is capable of determining amounts as small as 10<sup>-8</sup> g of this element. The uranium is fused in a melt of high-purity sodium fluoride, and the fluorescence produced on directing ultra-violet light at the cooled melt is measured by means of a photomultiplier tube. The fluorescence produced is related to the uranium content of the melt, but care is needed in applying this technique, since the uranium

fluorescence can sometimes be quenched by other constituents of the sample. Details of this technique and of the necessary equipment have been published.<sup>189</sup>

Macro amounts of uranium are conveniently determined by volumetric methods. A well tested procedure consists in passing the solution through a Jones reductor, which reduces the uranium to a mixture of the quadri- and tervalent forms.<sup>127</sup> An aeration step is then necessary to convert the tervalent uranium to the quadrivalent form before titration with either potassium permanganate or ceric sulphate. Since the reaction between quadrivalent uranium and ceric ions is slow at room temperatures, the usual procedure consists in the addition of a small excess of the titrant followed by titration back to the equivalence point with standard ferrous sulphate. The lead reductor is now, however, preferred to the Jones reductor, because it reduces the uranium to the quadrivalent form only and there is then no need for an aeration step. This reductor is also very easy to prepare and to maintain in working order. It has recently been critically examined and found to be useful for the direct analysis of aluminium - uranium alloys containing 20 per cent. of uranium.<sup>190</sup> This is a favourable alloy system, since with some alloys a preliminary separation of the uranium is essential. The lead reductor reduces several elements to lower valency states, and other elements, including bismuth, arsenic, antimony, silver, mercury and tellurium, are reduced to the metallic state, and the deposited metal tends to block the column. When a separation of the uranium from other sample constituents is necessary, there is no shortage of suitable procedures. Solvent-extraction methods are very convenient and, according to Scott,<sup>191</sup> ether is a suitable solvent for extracting uranium from solutions 3 M in nitric acid and M in ferric nitrate. By employing a volume of ether equal to the volume of sample solution, over 99 per cent. of the uranium is removed after three separate extractions. Other organic solvents have been used for extracting uranium from nitric acid solutions, and these include tributyl phosphate,<sup>192</sup> ethyl acetate<sup>193</sup> and mesityl oxide.<sup>189</sup>

High-precision spectrophotometry is also useful for determining the uranium content of metals and alloys containing uranium as the major constituent. Using the absorption of the uranyl ions, Bacon and Milner applied this technique to the determination of the uranium content of uranium metal<sup>194</sup> and uranium-base alloys containing molybdenum, titanium, niobium and zirconium.<sup>195</sup> The main advantage of this procedure is that no separations are required, but this method is not worth while unless many samples are to be analysed for uranium.

#### ZINC

The determination of minor alloying amounts of zinc in many non-ferrous alloys is readily accomplished by polarographic procedures. These methods are rarely direct, however, because zinc produces steps in most base electrolytes at voltages more negative than -1.0 volt against the S.C.E. The main advantage of the polarographic technique is that the separation of the interfering constituents need not be quantitative and, therefore, simple and rapid separations may be employed. For example, in the analysis of bronzes,<sup>196</sup> the copper is roughly precipitated from a nitric acid solution of the sample as cuprous iodide. After the removal of the precipitate, the zinc step is recorded from an ammonium hydroxide-ammonium chloride base solution. This separation process is not complete enough for the determination of zinc contents of less than 0.1 per cent, for which a longer procedure with hydrogen sulphide has to be used. Lingane<sup>89</sup> prefers to use controlled-potential electrolysis for the removal of copper in this determination. This is a very elegant technique, but it is not really suitable for routine analysis. This particular determination is now most readily carried out with the square-wave polarograph,<sup>126</sup> since a preliminary separation of the copper is not necessary and the nickel content of the alloy can be measured simultaneously.

A polarographic method has been used for many years in this country for the determination of the zinc content of aluminium alloys.<sup>197</sup> The separation of the zinc from certain interfering constituents is greatly facilitated by the use of an automatic centrifuge, and the zinc step is finally recorded from a sodium hydroxide base solution. This type of base electrolyte is not suitable for the determination of zinc in magnesium-base alloys because of the precipitation of magnesium hydroxide. Stross<sup>110</sup> recommends a method, however, in which the zinc step is recorded from a potassium thiocyanate base solution after the reduction of iron to the ferrous state. Any copper in the sample is precipitated as cuprous thiocyanate and any nickel gives a step, in this base, that is well separated from the zinc step. The zinc content of tin-base white-metal samples can be determined after the removal of

the tin as its volatile bromide and of group 2 elements as their insoluble sulphides.<sup>152</sup> The zinc step is finally recorded from an ammonium chloride - ammonium hydroxide base solution. For traces of zinc in refined lead,<sup>153</sup> most of the major constituent is removed from solution as its insoluble sulphate. Then the zinc step is recorded from a base solution containing ammonium sulphate, ammonium carbonate and ammonium hydroxide. The separation of the major constituent in a method for traces of zinc in metallic cadmium is most readily effected by controlled-potential electrolysis with a stirred mercury cathode.<sup>4</sup> For the determination of zinc in silver-base<sup>154</sup> and thorium-base<sup>155</sup> materials, no chemical separations are necessary.

Although polarographic methods are so convenient for the determination of zinc, alternative methods are available for the analysis of several types of alloys. The author<sup>156</sup> has described volumetric methods employing potassium ferrocyanide as the titrant and naphthidine as the indicator for the determination of the zinc content of many non-ferrous alloys. This technique requires that the zinc be separated from any other constituent that forms an insoluble ferrocyanide. The separation procedures are, therefore, necessarily longer and more complete than those used in the polarographic methods. With aluminium alloys, aluminium bronzes and white metals, the zinc is separated from interfering elements by hydrogen sulphide procedures, whereas with tin bronzes the separation is best accomplished with 8-hydroxyquinoline. Volumetric methods in which EDTA is used are now becoming available for the determination of the zinc content of non-ferrous alloys. In a method for zinc in aluminium alloys,<sup>200</sup> the zinc is first separated from many alloy constituents by treating the sample solution in the pH range from 4.5 to 7.0 with a sodium carbonate - sodium sulphide solution. The resultant precipitate contains nickel and copper in addition to the zinc. After the re-solution of the precipitate, potassium cyanide is added to form the cyanide complexes of the three constituents, followed by formaldehyde, which preferentially decomposes the zinc - cyanide complex. Then the zinc content of the solution is found by direct titration with EDTA. In an alternative method for this determination, an ion-exchange separation is employed for the removal of other alloy constituents from the zinc before the titration with EDTA is carried out.<sup>201</sup> General information on the use of anion-exchange resins for the separation of zinc in the analysis of several types of non-ferrous alloys is now available from the work of Miller and Hunter.<sup>202</sup>

### ZIRCONIUM

The determination of this element has been greatly simplified in recent years by the use of EDTA. A suitable volumetric procedure involves the addition of sufficient of a standard solution of EDTA to complex the zirconium and leave a small amount in excess. This excess is then determined by titration with a standard iron solution. Potassium benzohydroxamate<sup>203</sup> is used as the indicator for the pH range from 1.8 to 3.3 and for solutions with pH values from 3 to 7 sodium salicylate is satisfactory.<sup>204</sup> The spectrophotometric determination of the end-point is recommended, and by this means it is possible to determine directly the zirconium content of uranium - zirconium alloys when solutions of pH 2.3 are used.<sup>205</sup> The zirconium content of cerium - zirconium alloys can also be determined by a similar procedure.<sup>206</sup> These examples are, however, ideal cases, because both uranyl ions and cerous ions do not form complexes with EDTA in solutions of about pH 2. In many instances the prior separation of the zirconium from other alloying constituents is essential before the EDTA titrations can be applied. The precipitation of the zirconium as barium fluozirconate is very advantageous in alloy analysis, since the use of hydrofluoric acid is often essential for producing the complete solution of zirconium-containing alloys, and then the separation of the zirconium can be effected without having to remove the fluoride ions from the solution.<sup>206</sup> This method is suitable for the determination of zirconium in the presence of any of the following elements: uranium, titanium, niobium, tantalum, molybdenum, tungsten, lead, iron, copper and tin. The EDTA titration is also applicable after the separation of the zirconium from other constituents with organic precipitants, including benzoic, fumaric and mandelic acids.<sup>204</sup> The zirconium precipitate formed with benzoic acid can be dissolved in hydrochloric acid before the application of the titration. Sulphuric acid is suitable for the solution of the fumarate precipitate, and ammonium hydroxide is easily the best solvent for zirconium mandelate.<sup>187</sup>

An absorptiometric method is available for the determination of small amounts of zirconium in alloys. This is based on the strongly coloured lake formed by alizarin with this element, which is stable in acidic solutions. With the exception of hafnium, the lakes formed by alizarin with other cations are unstable under these conditions, so making this method almost specific for the determination of zirconium. The zirconium lake is formed in 1.5 N hydrochloric acid solutions on heating at a temperature greater than 85° C for a period of 2 minutes, and these conditions have been used for the determination of the zirconium content of magnesium-base alloys.<sup>207</sup> Sulphate ions, unfortunately, bleach the zirconium-alizarin lake, so that if it is necessary to use sulphuric acid in the solution of the sample, the amount of this reagent must be strictly controlled. In the development of a direct method for the determination of small amounts of zirconium in uranium-base alloys, Patterson<sup>127</sup> found that 0.01 N concentrations of sulphate ions could be tolerated. In the recommended method, therefore, the sample is dissolved in nitric acid and this solution is evaporated to fumes of sulphuric acid. The fuming process is continued to drive off the sulphuric acid and thereby reduce the concentration of sulphate ions to a very low value. Then the residue is dissolved in hydrochloric acid and the alizarin-zirconium lake is formed in this solution. It is necessary to adjust this solution so that the zirconium content is between 0.1 and 0.4 mg per 100 ml, otherwise Beer's law is not obeyed. Also when the ratio of uranium to zirconium exceeds a value of 500, a correction for the absorption due to uranyl ions is needed.

Thanks are due to Mr. A. A. Smales for several helpful suggestions.

#### REFERENCES

- Barker, G. C., and Jenkins, I. L., *Analyst*, 1952, **77**, 685.
- Lingane, J. J., "Electroanalytical Chemistry," Interscience Publishers Inc., New York, 1953.
- Milner, G. W. C., and Whittem, R. N., *Analyst*, 1952, **77**, 11.
- Lingane, J. J., *Anal. Chim. Acta*, 1948, **2**, 595.
- Mercer, R. A., and Williams, A. F., *J. Chem. Soc.*, 1952, 3399.
- Burstall, F. H., and Williams, A. F., *Analyst*, 1952, **77**, 983.
- Smales, A. A., and Loveridge, B. A., *Anal. Chim. Acta*, 1955, **13**, 566.
- Wilson, H. N., *Ibid.*, 1947, **1**, 330.
- Milner, G. W. C., and Woodhead, J. L., *Analyst*, 1954, **79**, 363.
- Wakkinnen, E., and Ringbom, A., *Anal. Chim. Acta*, 1955, **12**, 308.
- Milner, G. W. C., and Townend, J., *Analyst*, 1951, **76**, 424.
- Gwatkin, G. H. R., *Metallurgia*, 1952, **45**, 1122.
- Luke, C. L., *Anal. Chem.*, 1952, **24**, 1122.
- Price, J. B., and Payne, S. T., *Analyst*, 1949, **74**, 641.
- Corbett, J. A., *Ibid.*, 1953, **78**, 20.
- Claassen, A., Bastings, L., and Visser, J., *Anal. Chim. Acta*, 1954, **8**, 373.
- Pellowe, E. F., and Hardy, F. R. F., *Analyst*, 1954, **79**, 225.
- Bacon, A., *Ibid.*, 1952, **77**, 90.
- Sandell, E. B., "Colorimetric Determination of Traces of Metals," Second Edition, Interscience Publishers Inc., New York, 1950.
- Gentry, C. H. R., and Sherrington, L. G., *Analyst*, 1946, **71**, 432.
- Coppins, W. C., and Price, J. W., *Metallurgia*, 1953, **48**, 149.
- Osborn, G. H., and Stross, W., "Modern Methods for the Analysis of Aluminium Alloys," Chapman & Hall Ltd., London, 1949.
- Coppins, W. C., and Price, J. W., *Metallurgia*, 1952, **46**, 52.
- Clarke, S. G., and Evans, B. S., *Analyst*, 1929, **54**, 23.
- Holler, A. C., *Anal. Chem.*, 1947, **19**, 353.
- Luke, C. L., and Campbell, M., *Ibid.*, 1953, **25**, 1588.
- Luke, C. L., *Ibid.*, 1953, **25**, 674.
- "The Spectrochemical and Polarographic Analysis of Aluminium and its Alloys," The British Aluminium Co. Ltd., London, 1943.
- Cozzi, D., *Anal. Chim. Acta*, 1950, **4**, 204.
- Houligan, H. F., and Robinson, J. W., *Ibid.*, 1954, **10**, 281.
- Black, R. M., *Analyst*, 1950, **75**, 166.
- "A.S.T.M. Methods of Chemical Analysis of Metals," American Society for Testing Materials, Philadelphia, 1946, p. 246.
- Lingane, J. J., and Auerbach, C., *Anal. Chem.*, 1951, **23**, 986.
- Rodden, C. J., *J. Res. Natl. Bur. Stand.*, 1940, **24**, 7.
- Chase, O. P., *Anal. Chem.*, 1948, **20**, 902.
- Payne, S. T., *Analyst*, 1952, **77**, 278.
- Smales, A. A., and Pate, B. D., *Anal. Chem.*, 1952, **24**, 717.
- Naish, W. A., Clennell, J. E., and Kingswood, V. S., "Select Methods of Metallurgical Analysis," Chapman & Hall Ltd., London, 1953.

39. Rodden, C. J., *Editor*, "Analytical Chemistry of the Manhattan Project," McGraw-Hill Book Co. Inc., New York, 1950.
40. Luke, C. L., and Campbell, M. E., *Anal. Chem.*, 1952, **24**, 1056.
41. Adam, J. A., Booth, E., and Strickland, J. D. H., *Anal. Chim. Acta*, 1952, **6**, 462.
42. Vinci, F. A., *Anal. Chem.*, 1953, **25**, 1580.
43. Hall, C. J., *Analyst*, 1952, **77**, 318.
44. Fiander, S. J., *Ibid.*, 1955, **80**, 476.
45. Payne, S. T., British Non-ferrous Metals Research Association, London, Report No. 729, 1947.
46. Pletenev, S. A., Arefyeva, T. V., Tal, E. M., and Dubovitzkaja, E. I., *Zavod. Lab.*, 1946, **12**, 38.
47. Faucherelle, J., and Souchay, P., *Bull. Soc. Chim. France*, 1949, 722.
48. Schwarzenbach, G., "Komplexon-Methoden," B. Siegfried, A.G., Zofingen, Switzerland, 1950.
49. Cheng, K. L., *Anal. Chem.*, 1954, **26**, 1977.
50. Fritz, J. S., *Ibid.*, 1954, **26**, 1978.
51. Malát, M., Suk, V., and Ryba, O., *Chem. Listy*, 1954, **48**, 203.
52. Milner, G. W. C., and Edwards, J. W., unpublished work.
53. Strickland, J. D. H., Oliver, L. J., Allan, K., Strachan, J., and Spicer, G., C.C.I. Report No. TD/15, Parts 1 to 6, 1948, classified, to be published.
54. Naftel, J. A., *Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 407.
55. Spicer, G., and Strickland, J. D. H., Report CI/R50, 1952, classified, to be published.
56. —, —, Report CI/R54, 1952, classified, to be published.
57. Johnson, A., and Wright, H. A., Department of Atomic Energy Method No. 5, 1948.
58. Strickland, J. D. H., Department of Atomic Energy Method No. 9A, 1949.
59. Coursier, J., Huré, J., and Platzer, R., *International Conference for the Peaceful Uses of Atomic Energy, Geneva*, 1955, paper No. 344.
60. Philipson, T., *Lantbr Högsk. Ann.*, 1945, **12**, 251.
61. Highfill, J. P., New Brunswick Laboratory Report NBL 117, The Office of Technical Services, Department of Commerce, Washington, 25, D.C., 1955.
62. Bush, G. H., and Higgs, D. G., *Analyst*, 1951, **76**, 683.
63. Ford, E. G., *Canad. J. Tech.*, 1951, **29**, 61.
64. Nickelson, A. S., and Randles, J. E. B., "Polarographic and Spectrographic Analysis of High Purity Zinc and Zinc Alloys for Die Casting," H.M. Stationery Office, London, 1945.
65. Ferrett, D. J., Milner, G. W. C., Shalgovsky, H., and Slee, L. J., *Analyst*, 1956, **81**, 506.
66. Stross, W., *Metallurgia*, 1951, **43**, 145.
67. Ferrett, D. J., and Milner, G. W. C., *Analyst*, 1955, **80**, 132.
68. Zotta, M., *Gazz. Chim. Ital.*, 1948, **78**, 143.
69. Silverman, L., and Trego, K., *Analyst*, 1952, **77**, 143.
70. Wood, A. A. R., *Ibid.*, 1953, **78**, 54.
71. Milner, G. W. C., unpublished work.
72. Kolthoff, I. M., and Lingane, J. J., *J. Amer. Chem. Soc.*, 1940, **62**, 852.
73. Mills, E. C., and Hermon, S. E., *Metallurgia*, 1951, **44**, 327.
74. Mikula, J. J., and Codell, M., *Anal. Chem.*, 1955, **27**, 729.
75. "Chemical Analysis of Aluminium and its Alloys," The British Aluminium Co. Ltd., London, 1949.
76. Stross, W., and Stross, G., *Metallurgia*, 1952, **45**, 315.
77. Ovenston, T. C. J., and Parker, C. A., *Anal. Chim. Acta*, 1950, **4**, 142.
78. Dickens, P., and Maassen, G., *Arch. Eisenhüttenw.*, 1935, **9**, 487.
79. Yardley, J. T., *Analyst*, 1950, **75**, 156.
80. Milner, G. W. C., and Macara, R., Atomic Energy Research Establishment Report C/R 796, H.M. Stationery Office, London, 1951.
81. Chirnside, R. C., Cluley, H. J., and Proffitt, P. M. C., *Analyst*, 1947, **72**, 351.
82. Diehl, H., and Butler, J. P., *Anal. Chem.*, 1955, **27**, 777.
83. Mills, E. C., and Hermon, S. E., *Analyst*, 1951, **76**, 317.
84. Bacon, A., Royal Aircraft Establishment, Technical Note No. Met 32, 1946.
85. Hastings, J., McClarity, R. A., and Broderick, E. J., *Anal. Chem.*, 1954, **26**, 379.
86. Chilton, J. M., *Ibid.*, 1954, **26**, 940.
87. Ovenston, T. C. J., and Parker, C. A., *Anal. Chim. Acta*, 1950, **4**, 135.
88. Cluley, H. J., *Analyst*, 1954, **79**, 561.
89. Lingane, J. J., *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 429.
90. Milner, G. W. C., Wood, A. J., and Woodhead, J. L., *Analyst*, 1954, **79**, 272.
91. Milner, G. W. C., *Ibid.*, 1955, **80**, 77.
92. —, *Ibid.*, 1956, **81**, 367.
93. Onishi, H., and Sandell, E. B., *Anal. Chim. Acta*, 1955, **13**, 159.
94. Moeller, T., *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 270.
95. Milner, G. W. C., *Analyst*, 1951, **76**, 488.
96. Irving, H. M., and Rosotti, F. J. C., *Ibid.*, 1952, **77**, 801.
97. Nimer, E. L., Hamm, R. E., and Lee, G. L., *Anal. Chem.*, 1950, **22**, 790.
98. Flaschka, H., and Amin, A. M., *Mikrochim. Acta*, 1953, No. 4, 410.
99. Patrovsky, V., *Chem. Listy*, 1953, **47**, 1338.
100. Ovenston, T. C. J., and Parker, C. A., *Anal. Chim. Acta*, 1949, **3**, 277.
101. Edwards, F. H., and Gailer, J. W., *Analyst*, 1945, **70**, 365.
102. Jackson, H., Bailey, R. E., and Williams, L. H., *Metallurgia*, 1955, **51**, 309.
103. Meites, L., *Anal. Chem.*, 1952, **24**, 1374.
104. Wolfson, H., *Nature*, 1944, **153**, 375.
105. West, T. S., *Metallurgia*, 1951, **43**, 41.

106. Milner, G. W. C., and Townend, J., *Anal. Chim. Acta*, 1951, **5**, 584.
107. Milner, G. W. C., *Analyst*, 1945, **70**, 250.
108. —, *Metallurgia*, 1947, **36**, 287.
109. Stross, W., *Ibid.*, 1947, **37**, 49.
110. —, *Analyst*, 1949, **74**, 285.
111. Jones, R. H., *Ibid.*, 1946, **71**, 60.
112. Flaschka, H., and Huditz, F., *Z. anal. Chem.*, 1952, **137**, 172.
113. Bacon, A., *Metallurgia*, 1951, **44**, 207.
114. Challis, H. J. G., and Wood, D. F., *Analyst*, 1954, **79**, 762.
115. Sergeant, J. C., *Metallurgia*, 1953, **48**, 261.
116. Milner, G. W. C., and Groom, H., *Ibid.*, 1951, **44**, 271.
117. Spalenka, M., *Z. anal. Chem.*, 1947, **128**, 42.
118. Gibson, M., Atomic Energy Research Establishment Report C/R 350, 1949.
119. Lingane, J. J., and Karpus, R., *Anal. Chem.*, 1946, **18**, 191.
120. Davis, H. C., Royal Aircraft Establishment Report M 7880F, 1944.
121. Milner, G. W. C., Barnett, G. A., and Bacon, A., Atomic Energy Research Establishment Report C/R 1805, H.M. Stationery Office, London, 1956.
122. Bacon, A., and Milner, G. W. C., *Anal. Chim. Acta*, in the press.
123. Codell, M., Mikula, J. J., and Norwitz, G., *Anal. Chem.*, 1953, **25**, 1441.
124. Haslam, J., Russell, F. R., and Wilkinson, N. T., *Analyst*, 1952, **77**, 464.
125. Milner, G. W. C., *Ibid.*, 1945, **70**, 468.
126. Ferrett, D. J., and Milner, G. W. C., *Ibid.*, 1956, **81**, 193.
127. Treadwell, F. P., and Hall, W. T., "Analytical Chemistry," Ninth Edition, John Wiley & Sons Inc., New York, Volume II, 1942.
128. Flaschka, H., *Chemist Analyst*, 1953, **42**, 84.
129. Friibl, R., *Chem. Age*, 1955, **72**, 141.
130. Freund, H., and Levitt, A. E., *Anal. Chem.*, 1951, **23**, 1813.
131. Lauw-Zeche, A. B., Lord, S. S., and Hume, D. N., *Ibid.*, 1952, **24**, 1169.
132. Bacon, A., and Milner, G. W. C., *Anal. Chim. Acta*, 1956, **15**, 129.
133. Hastings, J., and McClarity, T. A., *Anal. Chem.*, 1954, **26**, 683.
134. Norwitz, G., Codell, M., and Verderame, F. D., *Anal. Chim. Acta*, 1953, **9**, 561.
135. Milner, G. W. C., Barnett, G. A., and Smales, A. A., *Analyst*, 1955, **80**, 380.
136. Thanheiser, G., *Mitt. K.-Wilh. Inst. Eisenforsch.*, 1940, **22**, 255.
137. Patterson, J. H., Argonne National Laboratory Report ANL 5410, Argonne National Laboratory, Lemont, Illinois, 1955.
138. Milner, G. W. C., and Wood, A. J., Atomic Energy Research Establishment Report C/R 895, H.M. Stationery Office, London, 1952.
139. Hunt, E. C., and Wells, R. A., *Analyst*, 1954, **79**, 345.
140. Seyfang, A. P., Springfield Chemical Services Memo. No. 51, Chemical Services Department, Springfield Works, 1955.
141. Milner, G. W. C., and Smales, A. A., *Analyst*, 1954, **79**, 425.
142. Davis, H. C., and Bacon, A., *J. Soc. Chem. Ind.*, 1948, **67**, 316.
143. Gentry, C. H. R., and Sherrington, L., *Ibid.*, 1946, **65**, 90.
144. Gibson, M., Atomic Energy Research Establishment Report C/R 521, 1950.
145. Morris, H. J., and Calverley, H. O., *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 447.
146. Rodills, G., *Bull. Biol. Pharm.*, 1934, **1**, 33.
147. Oberhauser, F., and Schormuller, J., *Z. anorg. Chem.*, 1929, **178**, 381.
148. Townend, J., and Milner, G. W. C., Department of Atomic Energy Method No. 47, classified.
149. Strickland, J. D. H., Department of Atomic Energy Method No. 26, classified.
150. —, Department of Atomic Energy Method No. 55, classified.
151. —, Department of Atomic Energy Method No. 106, classified.
152. "A.S.T.M. Methods of Chemical Analysis of Metals," American Society for Testing Materials, Philadelphia, 1946.
153. Diehl, H., and Butler, J. P., *Analyst*, 1952, **77**, 268.
154. Broadbank, R. W. C., and Winram, B. C., *Metallurgia*, 1953, **47**, 155.
155. Milner, G. W. C., and Woodhead, J. L., Atomic Energy Research Establishment Report C/R 1170, H.M. Stationery Office, London, 1953.
156. Cheng, K. L., *Anal. Chem.*, 1954, **26**, 1038.
157. Ringbom, A., *Acta Acad. Åbo*, 1943, **14**, 1.
158. Thomason, P. F., Perry, M. A., and Byerly, W. M., *Anal. Chem.*, 1949, **21**, 1239.
159. Mayer, A., and Bradshaw, G., *Analyst*, 1952, **77**, 154.
160. Kall, H. L., and Gordon, L., *Anal. Chem.*, 1953, **25**, 1256.
161. Banks, C. V., and Byrd, C. H., *Ibid.*, 1953, **25**, 416.
162. Fritz, J. S., and Ford, J. J., *Ibid.*, 1953, **25**, 1640.
163. Suk, V., Malát, M., and Ryba, O., *Chem. Listy*, 1954, **48**, 533.
164. Private communication from Chemical Services Dept., Springfield Works, U.K. Atomic Energy Authority.
165. Furby, E., Atomic Energy Research Establishment Report C/R 1435, 1954.
166. Milner, G. W. C., and Sneddon, G., Atomic Energy Research Establishment Report C/R 1740, 1955.
167. Milner, G. W. C., and Barnett, G. A., Atomic Energy Research Establishment Report C/R 1865, H.M. Stationery Office, London, 1956.
168. Levine, H., and Grimaldi, F. S., U.S. Atomic Energy Commission Report AECD 3186, 1950.

169. Milner, G. W. C., and Woodhead, J. L., Atomic Energy Research Establishment Report C/R 1400, H.M. Stationery Office, London, 1954.
170. Banks, C. V., and Edwards, R. E., *Anal. Chem.*, 1955, **27**, 947.
171. Milner, G. W. C., and Barnett, G. A., unpublished work.
172. Edwards, F. H., and Gailer, J. W., *Analyst*, 1944, **69**, 169.
173. Unpublished work of Bragg Laboratory, Janson Street, Sheffield.
174. Bishop, E., *Analyst*, 1953, **78**, 61.
175. Norwitz, G., and Codell, M., *Anal. Chim. Acta*, 1954, **11**, 38.
176. Kenyon, C., and Overston, T. C. J., *Nature*, 1951, **167**, 727.
177. Williams, F. R., and Whitehead, J., *J. Appl. Chem.*, 1952, **2**, 213.
178. Farnsworth, M., and Pekola, J., *Anal. Chem.*, 1954, **26**, 735.
179. Onishi, H., and Sandell, E. B., *Anal. Chim. Acta*, 1956, **14**, 153.
180. Glemser, O., Raulf, E., and Giesen, K., *Z. anal. Chem.*, 1954, **141**, 86.
181. Neal, W. T. L., *Analyst*, 1954, **79**, 403.
182. Milner, G. W. C., and Phennah, P. J., *Ibid.*, 1954, **79**, 414.
183. Potter, G. V., and Armstrong, C. E., *Anal. Chem.*, 1948, **20**, 1208.
184. Graham, R. P., and Hitchen, A., *Analyst*, 1952, **77**, 533.
185. Graham, R. P., Hitchen, A., and Maxwell, J. A., *Canad. J. Chem.*, 1952, **30**, 661.
186. Thompson, J. M., *Anal. Chem.*, 1952, **24**, 1632.
187. Milner, G. W. C., and Edwards, J. W., unpublished work.
188. Ferrett, D. J., and Milner, G. W. C., unpublished work.
189. Grimaldi, F. S., May, I., Fletcher, M. H., and Titcomb, J., Geological Survey Bulletin No. 1006, United States Government Printing Office, Washington, 1954.
190. Bacon, A., and Milner, G. W. C., Atomic Energy Research Establishment Report C/R 1813, H.M. Stationery Office, 1956.
191. Scott, T. R., *Analyst*, 1949, **74**, 486.
192. Wright, W. B., U.S. Atomic Energy Commission Report Y884, Carbide and Carbon Chemicals Co., Oak Ridge, Tennessee.
193. Guest, R. J., and Zimmerman, J. B., *Anal. Chem.*, 1955, **27**, 931.
194. Bacon, A., and Milner, G. W. C., Atomic Energy Research Establishment Report C/R 1637, 1955; part published in *Analyst*, 1956, **81**, 456.
195. ——, ——, Atomic Energy Research Establishment Report C/R 1749, H.M. Stationery Office, 1955.
196. Milner, G. W. C., *Metallurgia*, 1947, **35**, 265 and 307.
197. Stross, W., *Ibid.*, 1947, **36**, 163 and 227.
198. Patterson, J. H., and Banks, C. V., *Anal. Chem.*, 1948, **20**, 897.
199. Milner, G. W. C., *Anal. Chim. Acta*, 1952, **6**, 226.
200. Sergeant, J. C., *Metallurgia*, 1954, **50**, 252.
201. Rees, E. M., and Hartley, F., Atomic Weapons Research Establishment Report No. 0-65/54, 1955.
202. Miller, C. C., and Hunter, J. A., *Analyst*, 1954, **79**, 483.
203. Milner, G. W. C., and Edwards, J. W., *Ibid.*, 1955, **80**, 879.
204. Milner, G. W. C., and Phennah, P. J., *Ibid.*, 1954, **79**, 475.
205. Milner, G. W. C., and Sneddon, G., Atomic Energy Research Establishment Report C/R 1654, 1955.
206. Milner, G. W. C., and Barnett, G. A., Atomic Energy Research Establishment Report C/R 1780; *Anal. Chim. Acta*, 1956, **14**, 414.
207. Mayer, A., and Bradshaw, G., *Analyst*, 1952, **77**, 476.

ANALYTICAL CHEMISTRY GROUP  
ATOMIC ENERGY RESEARCH ESTABLISHMENT  
HARWELL, NR. DIDCOT, BERKS.

March 20th, 1956

## Determination of Copper in Steel

By L. J. A. HAYWOOD AND P. SUTCLIFFE

(Presented at the meeting of the Scottish Section on Friday, September 28th, 1956)

A method is described for the determination of copper in steel, in which the element is complexed with *biscyclohexanone oxalyldihydrazone* and the resulting blue colour is measured by means of the Spekker absorptiometer within the range 570 to 600 m $\mu$ . The procedure is very rapid, simple and direct, no extraction, filtration or other separation being necessary, and the accuracy of the results is at least equal to that attained by methods hitherto available.

Although not within the scope of the immediate investigation, it is considered that the method is also suitable for use with ferrous and with certain non-ferrous, e.g., aluminium, alloys.

METHODS commonly in use for the determination of copper in steels involve the separation as sulphide, either by the use of hydrogen sulphide or sodium thiosulphate. These are typified by the British Standard methods for copper in magnet alloys, by hydrogen sulphide separation,<sup>1</sup> and copper in carbon and low-alloy steels, by sodium thiosulphate.<sup>2</sup> The thiocyanate separation is generally unsuited to steel analysis, chiefly because of slow precipitation of copper thiocyanate when only small amounts of the element are present, and some solubility of the precipitate in the wash water.

Gravimetric methods of finishing involve the use of the relatively high conversion factor from oxide to metal of almost 80 per cent., with the objection of the extreme difficulty of decomposing the sulphide during ignition and converting it to oxide.

Methods involving use of sodium diethyldithiocarbamate, suitable for an absorptiometric finish, have been described,<sup>3,4</sup> but it is considered that the proposed method is both quicker and simpler, especially for routine batch determinations.

### EXPERIMENTAL

Recent publications<sup>5,6</sup> describing the use of *biscyclohexanone oxalyldihydrazone* in the detection and determination of small amounts of copper suggested, by virtue of the very large number of non-interfering elements, a possible application to the determination of copper in steels and ferrous metals generally. It appeared that no preliminary separations would be involved, which offered a rapid and direct method.

In order to check this theory and to prove the nature of the reactions, four B.C.S. steels were used, Nos. 252, 256, 253 and 235, containing, respectively, 0.11, 0.23, 0.495 and 0.98 per cent. of copper. Since it was desirable to have in solution not more than 100  $\mu\text{g}$  of copper, a 0.100-g sample of each steel was taken and dissolved in a mixture of 5 ml of hydrochloric acid and 5 ml of nitric acid. The solutions were cooled and 5 ml of a solution of citric acid (500 g of the crystalline acid dissolved in water and diluted to 1 litre) were added, followed by dilution to about 50 ml with distilled water. These solutions were then made just ammoniacal and diluted to 100 ml in a calibrated flask. From each, a 10-ml aliquot was taken by pipette and transferred to the 100-ml calibrated flask; then 20 ml of the reagent solution were added and water to make up to the mark. The solutions so formed were set aside for 10 minutes, then transferred to the Spekker absorptiometer with a water-to-air setting of 1.30 and an Ilford No. 606 filter, a 4-cm cell being used. The results, which were unchanged after the solution had been standing for several hours, were as follows—

B.C.S. No...	..	..	252	256	253	235
Copper, %	..	..	0.11	0.23	0.495	0.98
Absorptiometer reading	..	..	1.09	0.99	0.74	0.31

These readings appearing to be in good proportion, a series of synthetic standards was next prepared, high-purity iron (Hilger and Watts Ltd.) being used as a base, with additions of copper nitrate solution containing 0.01 g of copper per litre. The iron was treated in exactly the same way as described above for the steels, the standard copper solution being

added immediately before the reagent. The straight-line graph obtained, shown in Fig. 1, proved that the colour conformed to Beer's law.

One publication<sup>6</sup> specified the range of pH values within which the reaction should be carried out. Table I shows the results of a number of tests, the final adjustment of pH being made by the addition of diluted ammonia solution (ammonia solution, sp.gr. 0.880, diluted with 20 per cent. v/v of water). From this it is apparent that variations within the range 7.5 to 9.5 have no effect and, as this seemed to be a sufficiently wide range for all practical purposes, no further tests were made, except to confirm that at pH 13 the colour faded, whilst at pH 6.5 no colour was formed.

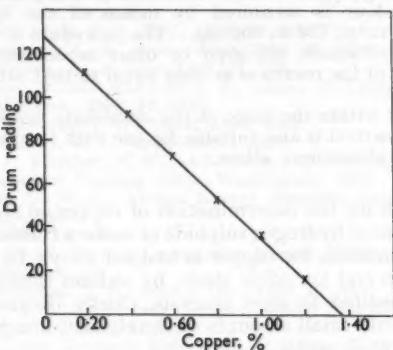


Fig. 1. Experimental confirmation of linearity of relation between drum reading and percentage of copper

TABLE I

EFFECT OF pH

The temperature of all solutions was between 22° and 28° C

B.C.S. steel	Copper, %	10 minutes after addition of reagent—		30 minutes after addition of reagent—		60 minutes after addition of reagent—	
		pH	absorptiometer reading	pH	absorptiometer reading	pH	absorptiometer reading
256	0.23	7.5	1.06	7.6	1.06	7.6	1.05
256	0.23	7.9	1.06	7.9	1.06	7.9	1.06
256	0.23	8.4	1.05	8.5	1.05	8.5	1.05
256	0.23	8.5	1.06	8.5	1.06	8.6	1.06
256	0.23	8.7	1.05	8.7	1.05	8.8	1.055
256	0.23	9.0	1.06	9.0	1.06	9.0	1.05
253	0.495	8.0	0.78	8.1	0.78	8.1	0.78
253	0.495	8.2	0.79	8.2	0.79	8.3	0.785
253	0.495	8.7	0.78	8.7	0.78	8.7	0.78
253	0.495	8.8	0.79	8.9	0.78	8.9	0.78
253	0.495	9.0	0.785	9.0	0.785	9.0	0.78
253	0.495	9.3	0.79	9.3	0.79	9.3	0.79
235	0.98	7.6	0.29	7.6	0.29	7.6	0.29
235	0.98	7.7	0.28	7.7	0.285	7.8	0.28
235	0.98	7.9	0.29	7.9	0.29	7.9	0.29
235	0.98	8.2	0.30	8.2	0.30	8.1	0.295
235	0.98	8.4	0.29	8.4	0.29	8.4	0.29
235	0.98	8.4	0.30	8.5	0.295	8.5	0.295
235	0.98	8.5	0.28	8.5	0.28	8.5	0.28
235	0.98	8.8	0.30	8.9	0.30	8.9	0.30
235	0.98	9.4	0.29	9.4	0.29	9.4	0.29
235	0.98	9.5	0.30	9.5	0.30	9.5	0.30

Table I also shows the results of variations in standing time after addition of reagent has been made, in periods up to 1 hour, and such range of temperature variation as may normally be encountered in laboratory practice. It is claimed that within the range specified,

i.e., 22° to 28° C, no significant variation in results need be expected, and that beyond the minimum standing time of 10 minutes, there is no variation of colour up to at least 60 minutes after addition of reagent.

Conditions for the reproducibility of results having been established, it was then necessary to determine the effect of possible interfering elements in the final coloured solution. Accordingly, 0.100-g amounts of various ions were placed separately into individual beakers, either as pure metal or from an equivalent weight of analytical-reagent grade salts, and brought into solution by a suitable means. The procedure already described was carried out on each sample and the colour of the copper complex was developed. The absorptiometer reading was noted for each solution and the results are listed in Table II.

TABLE II  
INTERFERING ELEMENTS

In each case the weight of interfering metal (or radical) was equivalent to  
100 per cent. of copper

Metal or radical	Copper added, %	Absorptiometer reading	Equivalent of copper, %	Copper added, %	Absorptiometer reading	Equivalent of copper, %
Fe	nil	1.29	0.01	0.50	0.78	0.51
Cr	nil	1.20	0.10	0.50	0.69	0.60
Co	nil	1.25	0.05	0.50	0.74	0.55
Sb	nil	1.30	0.00	0.50	0.79	0.50
Sn	nil	1.30	0.00	0.50	0.79	0.50
Pb	nil	1.30	0.00	0.50	0.79	0.50
Al	nil	1.30	0.00	0.50	0.79	0.50
Ba	nil	1.30	0.00	0.50	0.79	0.50
Bi	nil	1.30	0.00	0.50	0.79	0.50
W	nil	1.30	0.00	0.50	0.79	0.50
Ni	nil	1.29	0.01	0.50	0.78	0.51
Mn	nil	1.30	0.00	0.50	0.79	0.50
Ca	nil	1.30	0.00	0.50	0.79	0.50
Mg	nil	1.30	0.00	0.50	0.79	0.50
Zn	nil	1.30	0.00	0.50	0.79	0.50
Mo	nil	1.30	0.00	0.50	0.79	0.50
U	nil	1.295	0.005	0.50	0.79	0.50
Ag	nil	1.30	0.00	0.50	0.79	0.50
V	nil	1.30	0.00	0.50	0.79	0.50
$\text{CrO}_4^{2-}$	nil	1.28	0.02	0.50	0.77	0.52
$\text{SO}_4^{2-}$	nil	1.30	0.00	0.50	0.79	0.50
$\text{P}_2\text{O}_5$	nil	1.30	0.00	0.50	0.79	0.50
$\text{ClO}_4^-$	nil	1.30	0.00	0.50	0.79	0.50
$\text{NO}_3^-$	nil	1.30	0.00	0.50	0.79	0.50
$\text{Cl}^-$	nil	1.30	0.00	0.50	0.79	0.50

From these results, it is clearly seen that only iron, nickel, chromium and cobalt have any measurable effect. For most steels, the iron content will be virtually constant; in relatively few is it likely to be less than 0.070 g, and in any event could easily be compensated by additions of high-purity iron to make up to the equivalent of a 0.100-g sample if considered necessary. Interference due to nickel will be virtually negligible in all steels, including austenitic stainless types. In both instances, it is caused by the slight background colour of the element in solution.

This also applies to the elements chromium and cobalt, which, however, produce a more intense colour. If it is considered that this colour is too deep to be ignored, it can be allowed for by using either a correction graph or a difference reading, since it was found that the depth of colour was proportional to the percentage of element present. Additional investigation has provided a further alternative method of overcoming chromium interference almost completely, by oxidation of the element to the higher valency, when the yellow filter of the Spekker absorptiometer compensates for the colour of the chromate to such an extent that it is unnecessary to apply any correction to the readings obtained in determinations on austenitic stainless steels, the difference in the direct reading being under 0.01 per cent. of copper equivalent, or appreciably within the limits of experimental error.

In one or two instances, e.g., in presence of mercury and tin, when the metal was precipitated under the solution conditions required for determination, the precipitate was filtered off without affecting the result.

TABLE III  
DETERMINATION OF COPPER IN B.C.S. STEELS

B.C.S. No.	Composition	Certified value for copper, %	Copper by proposed method, %
246	Cr, 18.8%; Ni, 12.1%; Mo, 2.89%; Nb, 0.82%; V, 0.22%	0.13	0.12, 0.13
256	Cr, 2.34%; Mo, 0.53%; Mn, 1.21%	0.23	0.23, 0.23
214	Mn, 1.61%; Mo, 0.255%	0.24	0.24, 0.23
215	C, 0.93%; Si, 0.24%; Mn, 0.42%	0.08*	0.08, 0.08, 0.09
232	S, 0.067%; P, 0.076%	0.13*	0.13, 0.13
161/1	C, 0.83%; Mn, 1.00%	0.16*	0.16, 0.16
258	Cr, 3.07%; Mo, 0.43; V, 0.65%	0.18	0.18, 0.18
253	Ni, 2.92%; Mo, 0.95%; Co, 0.012%	0.495	0.49, 0.49, 0.49, 0.50
255	Cr, 0.96%; Ni, 0.57%; Mo, 1.41%	0.24	0.24, 0.24, 0.25
254	Cr, 0.53%; Ni, 2.08%; Mo, 1.29%; V, 0.52%	0.11	0.11, 0.12
257	Cr, 1.72%; Ni, 0.84%; Mo, 0.321%; Si, 0.37%	0.30	0.31, 0.32, 0.32, 0.30
167	W, 16.12%; Cr, 3.32%; Co, 4.35%; Mo, 0.55%	0.05*	0.065, 0.06

\* Refers to approximate figures issued with certificate.

The final table of results, Table III, shows the figures obtained for steels ranging from plain carbon to stainless and high-speed alloys, the results comparing most favourably with the published figures quoted on the analysis certificate included with the B.C.S. samples. The average time required for each single determination need not exceed 20 to 25 minutes, and batches of from five to twenty determinations can be carried out easily by one operator in from  $\frac{1}{2}$  to  $1\frac{1}{2}$  hours, including the time required for weighing.

### METHOD

#### REAGENTS—

When appropriate, reagents should be of recognised analytical grade.

*Hydrochloric acid, sp.gr. 1.16.*

*Nitric acid, sp.gr. 1.42.*

*Perchloric acid, sp.gr. 1.70.*

*Citric acid solution*—500 g of the crystalline acid dissolved in water and diluted to 1 litre.

*Ammonia solution, sp.gr. 0.880.*

*Copper reagent*—0.1 g of biscyclohexanone oxalyldihydrazone dissolved in 10 ml of industrial methylated spirit and 10 ml of hot water, diluted to 200 ml and filtered if necessary.

#### PROCEDURE—

Weigh a 0.1-g sample into a 150-ml conical beaker, add 5 ml of hydrochloric acid and 5 ml of nitric acid, and place the beaker on the edge of a hot-plate. In the presence of interfering amounts of chromium, add 5 ml of perchloric acid and evaporate to strong fumes to oxidise the chromium to the sexavalent state, as indicated by the deep orange-red colouration. When the sample has dissolved, or after the fuming with perchloric acid, remove the beaker from the hot-plate, and add about 50 ml of cold distilled water and then 10 ml of citric acid solution. Carefully add 10 ml of ammonia solution, cool to room temperature if necessary, and dilute to 100 ml in a calibrated flask. Return the solution to the original beaker and transfer a 10-ml aliquot by means of a pipette to the 100-ml calibrated flask. Add 20 ml of the copper reagent, dilute to 100 ml with cold distilled water and transfer to a dry 100-ml squat beaker. Set aside for 10 to 15 minutes, and then take a reading with the Spekker absorptiometer, having previously set the instrument with a water-to-air setting of 1.30, using H503 and Ilford No. 606 filters. The 4-cm cell will in general be found suitable for copper contents up to about 1.25 per cent. and the 1-cm cell up to approximately 5.5 per cent.

## NOTES—

1. If preferred, the fuming with perchloric acid may be carried out with all steels, regardless of chromium content, so unifying the procedure but adding a little extra time to the determination in low-chromium steels.
2. If an aliquot of one-hundredth of the original solution be used, samples containing up to 50 per cent. of copper can be analysed with reasonable accuracy.
3. With steels containing these higher percentages of copper, a proportionately more concentrated solution of the reagent is necessary.
4. The standard addition of 10 ml of ammonia solution was tested over a wide range of steels and, although the time taken to dissolve the samples varied considerably (with consequent variations in the amount of acid remaining), the pH invariably fell within the required range of 7.5 to 9.5.
5. The reagent solution keeps well and can conveniently be made up as a stock solution of four times the required concentration, being diluted with water for use.
6. All glassware before use must receive a final rinse with distilled water before being re-used or allowed to dry. Tap-water washings caused very erratic results, the reason for which was not investigated except that it does not appear to be a function of the pH of the water or the passage of the water through copper tubes.

## APPLICATION TO A SPOT-TEST ON A METAL SURFACE

As little as 0.12 per cent. of copper is clearly indicated as follows: put 1 drop of a 4 + 4 + 1 mixture of hydrochloric, nitric and citric acids on a clean metal surface; after about 45 seconds absorb the spot on a piece of dry filter-paper, and then hold it over an open bottle of ammonia solution to neutralise excess of acid. Add one drop of the stronger reagent solution to the spot, when the presence of copper is indicated by the formation of a blue colour. The intensity of the colour is roughly proportional to the amount of copper present and may be compared with a previously prepared set of standard test papers.

## CONCLUSIONS

The method offers a rapid and reliable procedure for the determination of copper in steels. It would appear to be suitable for use also with ferrous and various non-ferrous, e.g., aluminium, alloys, and has been successfully applied to lead-base alloys. Whilst a single determination can easily be carried out within 20 to 30 minutes, it is also eminently suited for batch routine determinations and the accuracy is at least as good as, and in many cases better than, that given by methods previously in use.

We are indebted to the Directors of Catton and Company Limited for permission to publish the results of this work, and to the members of the laboratory staff for encouragement and for their checking of the method under routine conditions.

## REFERENCES

1. British Standard 1121: Part 5. Copper in Permanent Magnet Alloys.
2. British Standard 1121: Part 14. Copper in Carbon and Low Alloy Steels.
3. Haywood, F. W., and Wood, A. A. R., "Metallurgical Analysis by means of the Spekker Photo-electric Absorptiometer," Adam Hilger Ltd., London, 1944, pp. 50 to 54.
4. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., "Applied Inorganic Analysis," John Wiley & Sons Inc., New York, 1953, p. 253.
5. Williams, T. R., and Morgan, R. R. T., *Chem. & Ind.*, 1954, 461.
6. Johnson, W. C., *Editor*, "Organic Reagents for Metals and Other Reagent Monographs," Fifth Edition, Hopkin & Williams Ltd., Chadwell Heath, Essex, 1955, pp. 31 and 32.

CATTON AND COMPANY LIMITED  
YORKSHIRE STEEL FOUNDRY  
HUNSLET, LEEDS, 10

First submitted, January 31st, 1956  
Amended, June 21st, 1956

# The Polarographic Determination of Chromium in Molybdenum-Chromium Alloys

By D. G. HIGGS

A method is described for the determination of chromium in molybdenum-chromium alloys. The range of composition 0 to 20 per cent. is covered by the use of two separate calibration curves (*a*) 0·05 to 1·5 per cent., and (*b*) 1·0 to 20 per cent., for which different sample weights are required. The diffusion-current curves are determined over the range -0·5 to -1·3 volts against a mercury pool and the polarograms thus obtained on a damped instrument are well formed and extremely easy to read.

MOST metals that can be determined by means of the polarograph have already been thoroughly investigated under most of the conditions in which they are likely to be associated, and chromium is no exception. The introduction of molybdenum as a basic metal for alloys is new and, to the best of my knowledge, no published method exists for the polarographic determination of chromium in the presence of molybdenum. A paper by Gokholstein<sup>1</sup> states that the reduction of chromate in *M* potassium hydroxide proceeds readily according to the formula—



whereas the reduction of  $\text{MoO}_4^{2-}$  can only proceed in an acid solution. This confirms the statement by Kolthoff and Lingane,<sup>2</sup> who state that molybdenum is not reduced in neutral or alkaline solutions, whilst chromium is reduced in a solution *M* with respect to sodium or potassium hydroxides at a half-wave potential of -0·86 volt against a saturated-calomel electrode. In an earlier paper<sup>3</sup> a method has been described, substantially that of Ridsdale,<sup>4</sup> for the chemical determination of chromium in molybdenum alloys; however, some of the chemical determinations referred to in the above-mentioned paper can be done more readily by the polarograph.

## EXPERIMENTAL

Preliminary experiments were carried out in which a known quantity of a standard chromium solution was added to each of four 1-g quantities of pure molybdenum metal. Solution was effected by adding 15 ml of 12*M* hydrochloric acid and 10 ml of 16*M* nitric

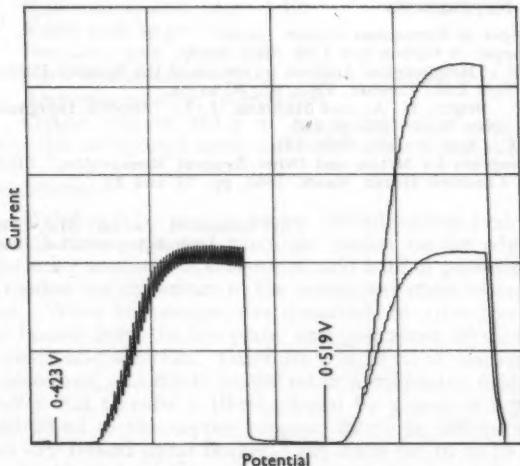


Fig. 1 (a). Typical undamped and damped polarograms due to the reduction of chromate in *M* sodium hydroxide solution containing 0·0021 *M* sodium molybdate

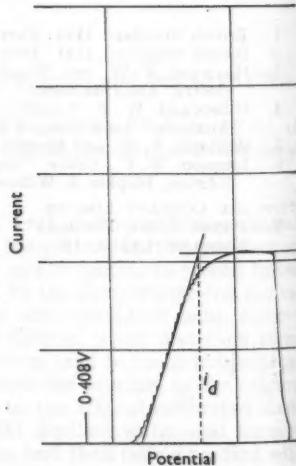


Fig. 1 (b). Method of measuring the diffusion current as represented by the dotted vertical line, *d*

acid; when the metal had completely dissolved, the solution was evaporated to dryness, and the residue was cooled. To the residue were added 15 ml of 5*M* sodium hydroxide and 25 drops of 100-volume hydrogen peroxide, and the resulting clear solution, after being boiled for 5 to 10 minutes, was cooled in a water bath. Then 1 ml of 1 per cent. w/v gelatin solution was added to the solution, which was diluted to 50 ml in a calibrated flask. This solution was transferred to a polarographic cell and deoxygenated with a stream of pure nitrogen for 5 minutes, after which polarograms were recorded between -0.5 and -1.3 volts against a mercury-pool electrode. Each polarogram rose steeply from the zero line to give a well formed trace and a plateau at the maximum diffusion current; only at great sensitivity did the plateau show a tendency to rise from the horizontal plane. A typical polarogram is shown in Fig. 1 (a), and the method of measuring the diffusion current can be seen from Fig. 1 (b). The results of these experiments are given in Table I.

TABLE I

## RELATIONSHIP BETWEEN CHROMIUM CONCENTRATION AND DIFFUSION CURRENT

Chromium added, μg per ml	Step height, units	Diffusion current, μA*	Diffusion current, μA per μg per ml	Mean value, μA per μg per ml
34	76.0	7.6	0.223	0.217
	37.0	7.4	0.217	
	36.0	7.2	0.212	
104	59.0	23.6	0.226	0.226
	59.0	23.6	0.226	
	47.0	23.5	0.226	
214	94.0	47.0	0.220	0.219
	46.5	46.5	0.217	
416	92.5	92.5	0.222	0.222
	46.0	92.0	0.221	
Mean = 0.221				

\* Corrected to μA for a sensitivity of 10 μA ≈ 100 divisions.

These results when plotted showed a linear relationship over the whole range; hence for a 1-g sample in 50 ml of solution a diffusion current of 89 μA would be obtained for an alloy containing 2 per cent. of chromium. In other words, for an instrument with a minimum sensitivity of 200 μA for full-scale reading, the highest alloy content measurable would be about 4.5 per cent. of chromium. To cover the range 0 to 20 per cent. of chromium it is obvious that two ranges of concentration are required, in order to reduce to the minimum the experimental errors involved. The two ranges chosen as most suitable were (A) 0.05 to 1.5 per cent. of chromium: a 1-g sample finally diluted to 50 ml, and (B) 1.0 to 20 per cent. of chromium: a 0.2-g sample finally diluted to 100 ml.

## PREPARATION OF CALIBRATION CURVES

*Range A: 0.05 to 1.5 per cent. of chromium*—To seven 1-g portions of molybdenum metal, contained in 250-ml squat beakers, add, respectively, 1, 2 and 3 ml of 0.01*N* potassium dichromate and 2, 3, 5 and 8 ml of 0.1*N* potassium dichromate; these volumes correspond to the values of 0.017, 0.051, 0.104, 0.34, 0.52, 0.86 and 1.39 per cent. of chromium. Add 5 ml of 12*M* hydrochloric acid and 15 ml of 6*M* nitric acid, cover each beaker and heat until solution of the metal is complete; remove the cover-glass, wash the underside with a jet of distilled water and evaporate the solution to dryness. Continue as described above under "Experimental." Set the instrument to the desired degree of sensitivity and record a polarogram between -0.5 and -1.3 volts against a mercury pool and use the damped wave for the determination of the diffusion current. The results obtained are given in Table II, and when plotted as the relationship between diffusion current and chromium concentration gave a straight line passing through the origin.

*Range B: 1.0 to 20.0 per cent. of chromium*—To six 0.2-g portions of molybdenum add, respectively, 1, 2, 3.5, 5, 10, 15 and 20 ml of 0.1*N* potassium dichromate, measured accurately from a burette; these volumes correspond to the values of 0.86, 1.73, 3.04, 4.33, 8.67, 13.0 and 17.3 per cent. of chromium. Add 2 ml of 12*M* hydrochloric acid and 10 ml of 6*M* nitric acid. Continue as previously described, but add 2 ml of gelatin solution and dilute the solution to a final volume of 100 ml in a calibrated flask. The results, shown in Table III, when plotted gave a straight line that passed through the origin.

TABLE II

CALIBRATION-CURVE RESULTS FOR THE RANGE 0·05 TO 1·5 PER CENT.  
OF CHROMIUM IN MOLYBDENUM

A 1-g sample diluted to 50 ml

Chromium added, %	Step height, units	Diffusion current, $\mu\text{A}^*$	Mean value, $\mu\text{A}$	Diffusion current, $\mu\text{A}$ per $\mu\text{g}$ per ml
0·052	51·0	2·55	2·52	0·247
	26·0	2·60		
	24·0	2·40		
0·104	46·0	4·60	4·60	0·219
	23·0	4·60		
0·34	78·0	15·6	15·6	0·229
	39·0	15·6		
	59·6	23·8		
0·52	46·0	23·0	23·0	0·225
	23·0	23·0		
	89·0	44·5		
1·04	44·5	44·5	44·5	0·212
	31·0	62·0		
1·39	30·9	61·8	61·9	0·223
Mean = 0·229				

\* Corrected to  $\mu\text{A}$  for sensitivity of 10  $\mu\text{A}$  = 100 divisions.

TABLE III

CALIBRATION-CURVE RESULTS FOR THE RANGE 1·5 TO 20·0 PER CENT.  
OF CHROMIUM IN MOLYBDENUM

A 0·2-g sample diluted to 100 ml

Chromium added, %	Step height, units	Diffusion current, $\mu\text{A}^*$	Mean value, $\mu\text{A}$	Diffusion current, $\mu\text{A}$ per $\mu\text{g}$ per ml
0·87	87·6	4·38	4·39	0·252
	44·0	4·40		
	43·9	4·39		
1·73	87·4	8·74	8·72	0·251
	43·6	8·72		
	43·5	8·70		
3·04	76·5	15·3	15·3	0·252
	38·0	15·2		
	30·6	15·3		
4·33	43·3	21·8	21·8	0·252
	54·5	21·8		
	43·4	21·7		
8·67	87·4	43·7	43·6	0·252
	43·6	43·6		
	21·7	43·7		
13·0	65·7	65·7	65·8	0·253
	32·9	65·8		
17·3	87·5	87·5	87·6	0·253
	43·8	87·6		
Mean = 0·252				

\* Corrected to  $\mu\text{A}$  for sensitivity of 10  $\mu\text{A}$  = 100 divisions.

#### METHOD

##### APPARATUS—

Polarograph—Tinsley, Model V3211. Capillary drop time of 1·59 seconds and mass "M" of mercury of 0·00370 g of mercury per second.

##### REAGENTS—

Hydrochloric acid, 12 M.

Nitric acid, 6 M.

Sodium hydroxide, 5 M.

Hydrogen peroxide, 100-volume.

Gelatin solution, 1 per cent. w/v.

## PROCEDURE—

Dissolve 1.00 g of sample in a mixture of 5 ml of 12 *M* hydrochloric acid and 15 ml of 6 *M* nitric acid contained in a 250-ml squat beaker (for a 0.2-g sample add 2 ml of hydrochloric acid and 10 ml of nitric acid). Heat gently, with a cover-glass over the mouth of the beaker, until the sample is completely dissolved; a clear solution free from precipitated molybdc oxide should be obtained. Remove the cover-glass, wash down the underside and the walls of the beaker with a jet of distilled water and finally evaporate the solution to dryness on an asbestos pad. Cool, wash down the sides of the beaker with 10 to 15 ml of cold water, add 25 drops of hydrogen peroxide and then 20 ml of 5 *N* sodium hydroxide (for a 0.2-g sample use 15 ml). Boil the solution for 10 minutes to ensure complete oxidation of the tervalent chromium to chromate. Cool, wash down the cover-glass and the sides of the beaker and transfer the solution to a 50-ml calibrated flask, add 1 ml of gelatin solution, dilute to the mark and mix thoroughly. (Use a 100-ml calibrated flask and 2 ml of gelatin solution for a 0.2-g sample.)

Transfer about 5 ml of the solution to a suitable polarographic cell, deoxygenate with a moderate stream of pure nitrogen for about 5 minutes, select the appropriate sensitivity range and record a polarogram between -0.5 and -1.3 volts against a mercury pool. Read off the percentage of chromium in the sample from the step height obtained and the appropriate calibration curve.

## RESULTS

The results, given in Table IV, of a series of determinations based on both sample weights show very good agreement with those obtained by the chemical method.

TABLE IV  
COMPARISON BETWEEN POLAROGRAPHIC AND CHEMICAL RESULTS FOR CHROMIUM  
IN MOLYBDENUM - CHROMIUM ALLOYS

Chromium found by	Polarographic method, %	Mean for result by polarographic method, %	Deviation from result by chemical method, %
Chemical method, % <i>With a 1.0-g sample—</i>			
0.023	0.023		
	0.025		+0.001
	0.026		
0.052	0.054		+0.002
	0.054		
	0.052		
0.059*	0.053		
0.054*	0.057		-0.01
	0.055		
	0.061		
0.26	0.25		-0.01
	0.24		
	0.25		
0.52	0.54		+0.02
	0.55		
	0.54		
0.84	0.82		-0.02
	0.82		
	0.83		
<i>With a 0.2-g sample—</i>			
0.92	0.91	0.91	-0.01
1.18	1.20	1.20	+0.02
2.26	2.32	2.32	+0.06
	2.70		
2.71	2.70		-0.01
	2.71		
	2.70		
5.24	5.16	5.16	-0.08
7.54	7.60	7.60	+0.06
13.9	13.7	13.7	-0.2
19.0	19.2	19.2	+0.2

\* This sample consistently showed evidence of segregation.

These results indicate the degree of reproducibility that may be obtained by this procedure. The drop-time may be considered quicker than is really desirable, but no difficulty was encountered throughout this investigation. The difference in slope of the two curves, as indicated by the two values for the diffusion current obtained for range A and B is not large and can easily be accounted for by the different concentrations of sodium molybdate in the solutions used. The method is more rapid than the chemical method referred to above,<sup>3</sup> fewer reagents are required and it has the added advantage that should a mishap occur during the final determination stage, a repeat on the remainder of the solution may readily be made.

#### CONCLUSIONS

A rapid method is presented for the determination of chromium in molybdenum-base alloys; it involves few operations and the final polarograms are extremely easy to measure.

The chromium curves cover the ranges 0·05 to 1·5 and 1·0 to 20·0 per cent. of chromium on different sample weights; both curves are straight lines that pass through the origin. Reproducibility is good and the accuracy is  $\pm$  2 to 3 per cent. for range A and  $\pm$  1 to 2 per cent. for range B.

Reproduced by permission of the Controller, H.M. Stationery Office.

#### REFERENCES

1. Gokholstein, Ya. P., *Trudy Komissii Anal. Khim., Akad. Nauk. S.S.R.*, *Otdel. Khim. Nauk.*, 1949, **2**, 54; *Chem. Abstr.*, 1950, **44**, 9271.
2. Kolthoff, I. M., and Lingane, J. J., "Polarography," Interscience Publishers Inc., New York, 1941.
3. Bush, G. H., and Higgs, D. G., *Analyst*, 1955, **80**, 536.
4. "Analoid System of Analysis," Ridsdale & Co., Ltd., 3 Wilson Street, Middlesborough, England.

ARMAMENT RESEARCH AND  
DEVELOPMENT ESTABLISHMENT  
FORT HALSTEAD, NR. SEVENOAKS, KENT

March 13th, 1956

## Geochemical Field Methods for the Determination of Tungsten and Molybdenum in Soils

By A. A. NORTH

Geochemical prospecting methods for the determination of trace amounts of tungsten and molybdenum in soils by means of dithiol (toluene-3:4-dithiol) are described.

The soils are fused with a modified carbonate flux, the melts are leached with water, and aliquots of the aqueous extracts are used for the determinations. At high temperatures (about 100° C) the blue-green tungsten - dithiol complex is extracted selectively into isoamyl acetate from concentrated hydrochloric acid solutions containing stannous chloride, which prevents the formation of the molybdenum complex. At low temperatures (20° to 25° C) the yellow-green molybdenum - dithiol complex is extracted selectively into isoamyl acetate from dilute hydrochloric acid solutions. Determinations are made by visual comparison of the colour intensities of the dithiol complexes with standards.

The field methods, as described, can be used for the determination of tungsten over the range 4 to 400 p.p.m., and molybdenum over the range 1 to 100 p.p.m. in soils. Simple modifications of the methods permit the determination of greater amounts of the trace metals.

SOILS, water, stream sediments and plants in the neighbourhood of ore bodies frequently contain high or anomalous amounts of the elements constituting the ore compared with the normal or background values in similar materials in barren regions. This is consequent on the primary geochemical dispersion of the elements at the time of mineralisation, and their subsequent redistribution by physical or mechanical, chemical and biochemical agencies to give secondary dispersions. Geochemical prospecting methods based on the analysis of soils

81  
this  
tly  
ves,  
not  
late  
to  
hap  
may  
  
base  
ure.  
ium  
gin.  
per  
  
auk,  
1941.  
land.  
  
1956  
  
of

collected systematically are particularly valuable for the location of sub-outcropping ore bodies, since secondary dispersions can arise in both residual and non-residual cover. The number of samples collected is usually very large, so that acceptable analytical methods must be rapid, simple and inexpensive; but, as the magnitudes of anomalous values are frequently many times greater than background values, analytical methods of great accuracy are not always essential.

Paper-chromatographic methods of analysis applicable to geochemical prospecting have been described,<sup>1</sup> but attempts to utilise this technique for the determination of trace amounts of tungsten and molybdenum in soils were unsuccessful. Fusion of soils with the alkali flux, necessary to obtain solution of these trace metals, resulted in such a high concentration of alkali-metal salts in the aqueous extracts of melts applied to paper strips that chromatographic separations were vitiated. Considerable dilution of the extracts before the application of aliquots to paper strips overcame this difficulty, but resulted in too great a loss of sensitivity.

Field methods based on laboratory colorimetric procedures with thiocyanate and stannous chloride have been described for the determination of trace amounts of tungsten in soils,<sup>2</sup> and of molybdenum in soils and rocks.<sup>3</sup> These methods permitted the detection of 10 p.p.m. of tungsten and 1 p.p.m. of molybdenum in the original material. However, a preliminary investigation of the distribution of tungsten in the neighbourhood of a mineralised shear zone indicated that a field method with better discrimination and greater sensitivity to cover the range 5 to 40 p.p.m. of tungsten in soils was required. The use of toluene-3:4-dithiol (dithiol) for the colorimetric determination of tungsten and molybdenum, as an alternative to the thiocyanate - stannous chloride methods, was therefore investigated.

Since Hamence,<sup>4</sup> Miller and Lowe<sup>5</sup> and Miller<sup>6,7,8</sup> described the use of dithiol for the detection of molybdenum and tungsten, many workers have used this reagent for the quantitative determination of these elements. Methods have been published for the determinations of molybdenum in plant materials<sup>9</sup> and of molybdenum and tungsten in steels,<sup>10,11,12</sup> pharmaceuticals,<sup>13</sup> titanium metal<sup>14</sup> and in biological materials.<sup>15</sup> The methods generally fall into one of two groups. The first involves time-consuming precipitation of the dithiol complex from sulphuric acid solution, often at a carefully controlled pH and salt concentration, followed by the extraction of the complexes into an organic solvent. The second involves the formation and concurrent extraction of the molybdenum - dithiol or tungsten - dithiol complex into *isoamyl* or *n*-butyl acetate from hydrochloric acid solution.

The latter procedures possess the advantages of both speed and simplicity, and it proved possible to modify them for use in the field.

#### EXPERIMENTAL

The use of a flux containing equal amounts of sodium carbonate and potassium nitrate has been recommended for the decomposition of samples, for the determination of molybdenum in soils and rocks<sup>3</sup>; but the large amount of nitrite produced by decomposition of the nitrate during the gentle fusion interfered with the determination of molybdenum by means of dithiol. A flux containing five parts, by weight, of sodium carbonate, four parts of sodium chloride and one part of potassium nitrate has been used for the determination of tungsten in soils.<sup>2</sup> The use of this flux was found to be satisfactory for the decomposition of soils, for the determination of both tungsten and molybdenum, since interference from the small amounts of nitrite produced could be overcome. The sodium chloride present served to reduce the fusion temperature of the flux, so facilitating fusion over camping stoves used in the field.

For determinations in the field, 0.25 g of soil sample was fused in a nickel crucible with 1.25 g, the minimum permissible quantity, of flux. The crucibles were large enough (3 cm × 3 cm) to allow the melts to be leached directly by adding hot water to the crucibles. After stirring with glass rods to free the melts from the crucibles, the slurries obtained were transferred to graduated test-tubes and the volumes were adjusted to 5 ml. The tubes were then heated by immersion in a boiling-water bath for 10 minutes and were shaken occasionally to ensure the complete break up of the melts. The tubes were set aside to cool and to allow insoluble matter to settle out. Aliquots of the supernatant liquors were taken for the determination of tungsten or molybdenum.

Decomposition of the soils by fusion with potassium hydroxide was investigated, since the melts obtained could be leached more readily than those resulting from the use of the

carbonate flux. Very poor recoveries of tungsten and molybdenum resulted, possibly owing to their occlusion in the leached residues, which contained a considerable amount of nickel from the crucible. Errors due to the retention of tungsten or molybdenum in the leached residues were found to be negligible when the modified carbonate flux was used and, as the attack on the crucibles was much less severe, they could be used for a greater number of fusions.

#### FORMATION AND EXTRACTION OF THE TUNGSTEN - DITHIOL COMPLEX—

The field method evolved for the determination of tungsten was based on Miller's procedure for the detection of tungsten. Miller<sup>8</sup> found that the blue-green tungsten - dithiol complex could be extracted selectively from solutions that were at least 10 N with respect to hydrochloric acid, and that selectivity was associated with the addition of the reagent, toluene-3:4-dithiol, in *n*-butyl acetate or *isoamyl* acetate. Interference from trace amounts of molybdenum and rhenium and moderate amounts of iron and other elements was prevented by warming the acid test solutions with stannous chloride for a few minutes before the addition of the reagent.

For simplicity in the field and, in order that the minimum amount of apparatus was required, it was desirable that the formation and extraction of the tungsten - dithiol complex be carried out in test-tubes. Preliminary experiments with 16-mm × 150-mm test-tubes showed that it would be necessary to extract the tungsten from 0·5-ml aliquots of the carbonate leach liquors into small volumes about 0·5 ml of ester, in order to achieve the required sensitivity. The use of larger aliquots of the leach liquors was impracticable, owing to the difficulty of manipulating in test-tubes the correspondingly larger volumes of the test solutions obtained after acidification. Although the rate of the reaction between tungsten and dithiol is faster at higher temperatures, Miller recommended that the formation and concurrent extraction of the tungsten complex be carried out at 70° C, in order to minimise the loss of ester by evaporation. Experiments with 0·5 ml of ester containing dithiol for the extraction of the complex at 70° C showed that the loss of ester was significant and variable, so that attempts to determine the tungsten by comparison of the colour intensities of the ester layers with standards were vitiated. The use of a comparatively large volume of ester, such that evaporation losses were insignificant, made it impossible to achieve the required sensitivity. The difficulty was overcome by completing the reaction in a shorter time at a higher temperature, so that practically all of the ester was volatilised. A small measured volume of a suitable organic solvent was then added to give organic layers of sensibly constant volume.

Experiments showed that tungsten could be extracted quantitatively as the dithiol complex from 0·5-ml aliquots of carbonate leach liquors after the addition of 5 ml of a 2 per cent. stannous chloride solution in hydrochloric acid, which rendered the test solution 10 N with respect to the acid. It was found unnecessary to add phosphoric acid to prevent the precipitation of the trace amounts of tungsten as tungstic acid. (Stable 0·006 M tungstate solutions in concentrated hydrochloric acid have been prepared.<sup>16</sup>) Immersion of the lower halves of the test-tubes in a boiling-water bath, and heating the test solutions containing stannous chloride for 4 minutes before the additions of dithiol, reduced any molybdenum or other interfering elements present to lower unreactive valency states. The heating also destroyed the nitrous acid that was produced when the leach liquor was acidified. The addition of more than 100 mg of stannous chloride was found to be unnecessary and undesirable, as tin reacts partly with dithiol in hydrochloric acid solutions to form a complex soluble in organic solvents. The use of 5 ml of a 10 per cent. solution of stannous chloride in hydrochloric acid gave rise to a pale yellow coloration that masked the colour due to very small amounts of tungsten.

After reduction of the interfering elements, 0·5 ml of a 1 per cent. solution of dithiol in *isoamyl* acetate was added, and the tubes were shaken cautiously. Heating in the boiling-water bath was continued, and the tubes were shaken gently every 3 or 4 minutes to facilitate the formation of the tungsten - dithiol complex. The ester was partly miscible with the acid test solution, partly hydrolysed and partly volatilised, so that after about 15 minutes only a globule remained. Heating was not prolonged further, otherwise, the globule containing the tungsten complex, and excess of dithiol sank and became enmeshed in the precipitated silica at the bottom of the tubes. Too vigorous shaking during the course of the reaction was avoided for the same reason. On cooling, the solubility of the ester in the test solution

decreased, and the size of the globule increased until a layer of ester about 1 mm deep was formed. If the mixture was set aside for several hours, the volume diminished owing to slow hydrolysis of the ester. This was avoided by the addition of 0.5 ml of kerosene that had been decolorised by treatment with charcoal. The addition of water-white kerosene to the test-tubes, as soon as their contents were cool, gave a layer, the volume of which was sensibly constant, containing the blue-green tungsten - dithiol complex. The depth of the layer (4 to 5 mm) allowed the determination of the tungsten to be readily made by visual comparison of the colour intensities with standards against a white background. Addition of the kerosene to the hot solution was avoided, since gentle shaking to mix the ester and kerosene then led to the formation of an emulsion.

Attempts to use *n*-butyl acetate instead of the less volatile *isoamyl* acetate were unsuccessful, since the time of reaction from the addition of the reagent to the formation of the globule was insufficient for the complete formation of the tungsten - dithiol complex. It was necessary to use *isoamyl* acetate of analytical-reagent grade, b.p. 138° to 140° C (80 to 85 per cent. *isoamyl* acetate and 15 to 20 per cent. of active amyl acetate). Other grades contained appreciable amounts of more volatile constituents and gave tars that masked the colour of the tungsten complex.

The 1 per cent. dithiol solution was prepared by warming a 1-g ampoule at 30° to 40° C until the reagent melted, and then dissolving the dithiol in 100 ml of *isoamyl* acetate. The solution, if kept cool, could be used satisfactorily for 2 to 3 days, or until it showed a pale yellow coloration due to decomposition of the reagent. Bagshawe<sup>12</sup> found the formation of the tungsten - dithiol complex less sensitive to the staleness of the reagent solution than the molybdenum complex, probably owing to stannous chloride reducing oxidation products of the reagent.

#### PREPARATION OF STANDARDS

Standards were prepared by the procedure described above for the formation and extraction of the tungsten - dithiol complex, suitable aliquots of fresh standard tungstate solutions being used. A standard solution containing 100 µg of tungsten per ml was prepared by dissolving 0.09 g of sodium tungstate dihydrate in water and diluting to 500 ml. This solution was then diluted with water to give solutions containing 1 µg and 10 µg of tungsten per ml; 0.1 to 1.0-ml aliquots of these two solutions were used for the preparation of standards. Aliquots larger than 1.0 ml could not be used, otherwise the acid concentration of the solutions, after the addition of 5 ml of 2 per cent. stannous chloride in concentrated hydrochloric acid, was too low for the complete extraction of the tungsten complex. The standards prepared covered the range 0.1 µg to 10 µg of tungsten, corresponding to 4 to 400 p.p.m. of tungsten in soils. The blue-green tungsten - dithiol complex was stable in kerosene solution for at least a week. A set of standards could be kept for some time, provided that evaporation was prevented by plugging the tubes with cotton-wool. It was possible to extend the range of the method by using additional standards containing up to 20 µg of tungsten or, preferably, by using smaller aliquots of the carbonate leach liquors for the determinations.

#### INTERFERENCES

The only interfering element likely to be present in the test solutions was molybdenum. Heating the acid test solutions containing stannous chloride before the addition of the dithiol reagent solution suppressed the formation of the coloured molybdenum complex. When less than 10 µg of molybdenum were present in the test solution, no yellow-green coloration due to the molybdenum complex could be detected in the ester - kerosene layer, whilst 0.1 µg of tungsten gave a perceptible blue-green coloration. When larger amounts were present, for example 50 µg of molybdenum, a pale yellow-green coloration was obtained in the organic layer equivalent to 1 per cent. of the molybdenum reacting to give the normal molybdenum - dithiol coloured complex; but determinations could still be made, provided that the molybdenum concentration was less than 50 times that of the tungsten. Hence, for geochemical prospecting purposes, the method for the determination of tungsten in soils was not subject to interference from molybdenum.

Large amounts of iron would have interfered with the determinations, but fusion of the soils with the carbonate flux and aqueous leaching of the melts separated tungsten from iron and other elements that form insoluble hydroxides. When treating soils of high copper content, some of the copper passed into the carbonate leach liquors and would have interfered

but for the preliminary heating with stannous chloride, which prevented the formation and dispersion of the insoluble black copper - dithiol complex in the ester. The preliminary heating with stannous chloride would also prevent interference from elements such as arsenic, which suppress the reaction between tungsten and dithiol, but these elements would not normally be present in soils in sufficient quantity to interfere.

Nitrites decompose dithiol, but the nitrite present in the leach liquors was destroyed on acidification and heating. Although on addition of hydrochloric acid to the leach liquors, gelatinous silicic acid separated out, no interference due to the occlusion of tungstate or tungstic acid was encountered.

#### METHOD FOR TUNGSTEN

##### REAGENTS—

*Flux*—A mixture of 5 parts by weight of sodium carbonate, 4 parts of sodium chloride and 1 part of potassium nitrate, ground to pass through an 80-mesh sieve.

*Hydrochloric acid, sp.gr. 1.18.*

*Stannous chloride*—Dissolve 10 g of stannous chloride,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , in concentrated hydrochloric acid, warm to give a clear solution, and make up to 500 ml with more acid.

*isoAmyl acetate*—Analytical-reagent grade.

*Toluene-3:4-dithiol*—Melt the contents of a 1-g ampoule at 30° to 40° C, and dissolve the reagent in 100 ml of *isoamyl acetate*.

*Kerosene, water-white.*

*Standard tungstate solution*—Prepare a solution containing 100  $\mu\text{g}$  of tungsten per ml by dissolving 0.09 g of pure sodium tungstate,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , in 500 ml of water.

##### PROCEDURE—

Mix 0.25 g of soil (-80 mesh) with 1.25 g of flux in a 3-cm  $\times$  3-cm nickel crucible, and heat to obtain a quiet melt. Cool, add 3 ml of hot water, and preferably set aside overnight, or use a glass rod and heat gently to free the melt from the crucible. Transfer the contents of the crucible to a graduated test-tube, wash out the crucible with two small volumes of water, and then make up to the 5-ml mark on the tube. Heat the tube in a boiling-water bath for 10 minutes to ensure the complete break-up of the melt. Set the tube aside to cool, and to allow insoluble matter to settle out. Transfer a 0.5-ml aliquot of the supernatant liquor to a dry 16-mm  $\times$  150-mm test-tube, and then add 5 ml of stannous chloride solution in concentrated hydrochloric acid. Heat the tube in a boiling-water bath for 4 minutes to reduce any interfering elements present. Then add 0.5 ml of *isoamyl acetate* containing dithiol, and shake the tube occasionally to facilitate the formation of the tungsten complex. After heating for about 15 minutes, when most of the ester has been hydrolysed, or volatilised and only a globule remains, remove the tube from the boiling-water bath. When cool, add 0.5 ml of water-white kerosene, and shake gently to mix the ester and kerosene. Compare visually against a white background the colour intensity of the blue-green tungsten - dithiol complex in the ester - kerosene layer with standards.

TABLE I

#### DETERMINATION OF TUNGSTEN IN SOILS BY LABORATORY AND FIELD METHODS

Sample No.	Tungsten found by field method, p.p.m.	Mean, p.p.m.	Tungsten found by laboratory method, p.p.m.
1	8, 8, 8, 8, 6	8	5.5
2	5, 8, 10, 8, 9	8	7.0
3	5, 6, 8, 10, 9	8	8.0
4	10, 10, 10, 10, 10	10	8.0
5	18, 20, 22, 18, 18	19	12.5
6	16, 20, 22, 18, 20	19	14.0
7	20, 22, 22, 22, 24	22	15.0
8	26, 24, 30, 28, 26	27	24.0
9	24, 28, 30, 28, 30	28	24.0
10	28, 32, 36, 40, 40	35	25.5
11	28, 28, 30, 32, 32	30	29.0
12	28, 32, 36, 38, 40	35	30.5
13	30, 40, 44, 48, 48	42	36.5
14	40, 48, 48, 52, 56	49	44.0

## RESULTS

The tungsten contents of 14 soils, collected in the neighbourhood of a mineralised shear zone, were determined. The results for five replicate determinations by the field method are given in Table I, together with the results obtained by a laboratory method.

No other soils containing anomalous amounts of tungsten were available for testing. To assess the accuracy of the field method for the determination of amounts up to 400 p.p.m. of tungsten in soils, known amounts of tungsten were added to a soil and the enriched samples were analysed. The calculated values for the standard deviations and analytical results are given in Table II.

TABLE II

## ACCURACY OF THE FIELD METHOD FOR THE DETERMINATION OF TUNGSTEN

Known tungsten content, p.p.m.	Tungsten found, p.p.m.	Standard deviation
33	36, 32, 30, 34, 30	2.7
58	60, 56, 60, 48, 56	5.4
108	120, 70, 120, 110, 120, 110, 110, 110, 120, 110, 140	15.9
208	200, 200, 200, 220, 200, 220, 200, 220, 200, 220	10.7
408	400, 400, 400, 360, 440	24.0

## EXPERIMENTAL

## FORMATION AND EXTRACTION OF THE MOLYBDENUM - DITHIOL COMPLEX—

Bagshawe and Truman<sup>12</sup> have described suitable conditions for the selective extraction of the yellow-green molybdenum - dithiol complex into *isoamyl acetate*. They recommended temperatures between 20° and 25° C for the formation and extraction of the complex from hydrochloric acid solutions of specific gravity 1.06. When more concentrated acid solutions were used, or at temperatures higher than 30° C, the tungsten - dithiol complex was also extracted. The presence of a small amount of hydroxylamine, to reduce oxidation products of dithiol, ensured the complete formation of the molybdenum complex; too much hydroxylamine interfered possibly owing to reduction of the molybdenum.

Preliminary experiments indicated the general suitability of the extraction procedure of Bagshawe and Truman as the basis of a simple field method for the determination of molybdenum in soils. It was found possible, using 0.5 ml of a fresh 1 per cent. solution of dithiol in *isoamyl acetate*, to extract molybdenum quantitatively from 4 or 5 ml of dilute molybdate solution, 4 N with respect to hydrochloric acid, that contained as much as 50 mg of hydroxylamine hydrochloride. The reactions could be carried out conveniently in 16-mm × 150-mm test-tubes, since after the mixture had been shaken to facilitate the formation and extraction of the yellow-green molybdenum - dithiol complex, the ester separated on standing to give a clear layer that did not need clarifying. The initial test-tube experiments with pure standard molybdate solutions indicated that an adequate sensitivity, 1 p.p.m. of molybdenum in soils, could be achieved: provided that the molybdenum complex could be extracted into 0.5 ml of ester from 2-ml aliquots of soil solutions, obtained by fusing 0.25 g of soil with an alkali flux and leaching the melts with 5 ml of water. It was found, however, that test-tubes could not be used for the extraction of molybdenum from soil solutions, owing to the interference of gelatinous silicic acid, which was precipitated when aliquots of leach liquors were acidified. After the test solutions had been shaken with dithiol in *isoamyl acetate*, and the tubes had been set aside to allow the phases to separate, the silicic acid frequently prevented drops of the ester from coalescing. The ester layer could be clarified, however, by separating the phases and washing the ester with concentrated hydrochloric acid. For simplicity in the field, separating funnels made by sealing glass taps to the bottoms of 16-mm × 150-mm test-tubes were used for the formation and extraction of the molybdenum complex from test solutions. Then, after the aqueous phase had been drained off and the ester clarified, the amount of molybdenum present could be determined by visual comparison of the colour intensity of the ester layer with standards prepared in 16-mm × 150-mm test-tubes. When 0.5 ml of dithiol solution in *isoamyl acetate* was used for the extraction of standard amounts of molybdenum, it was necessary to use 0.6 ml of ester containing dithiol for the extraction of molybdenum from acidified soil solutions. Then, owing to the slight miscibility of the ester with concentrated hydrochloric acid, the volume of the ester

phase was reduced to 0·5 ml on clarification by shaking for 30 seconds with 4 ml of acid. As the ester hydrolysed slowly while in contact with the concentrated acid, it was necessary to make comparisons with standards within a few minutes of clarifying the ester.

The nitrite present in aqueous extracts of melts obtained by fusion of soils with mixed carbonate - nitrate fluxes, if not previously destroyed, would have reacted with dithiol and interfered with the extraction of the molybdenum complex. Interference from this source was prevented by adding hydroxylamine hydrochloride to decompose the nitrous acid present in acidified soil extracts. The hydrochloride was added in amounts that were slightly in excess of those required for the decomposition of the theoretical maximum amounts of nitrite that could be formed during the fusions. It was found, however, that the efficiency of the field procedure for the extraction of the molybdenum - dithiol complex was inconsistent, and frequently very low, when a flux containing equal amounts of sodium carbonate and potassium nitrate had been used for the decomposition of the soils. Investigation showed this to be due to variations in the amount of nitrite formed during the fusions, leading in some cases to the presence of an intolerable excess of hydroxylamine hydrochloride.

The difficulty of regulating the excess of hydroxylamine was obviated by using 1·25 g of a flux containing five parts by weight of sodium carbonate, four parts of sodium chloride and one part of potassium nitrate for the decomposition of the soils. Then, 50 mg of hydroxylamine hydrochloride was more than sufficient to decompose the maximum amount of nitrite that could be present in 2-ml aliquots from 5 ml of leach liquors. The excess of hydroxylamine was always sufficient to prevent interference from oxidation products of dithiol, but insufficient to interfere with the formation of the molybdenum complex. For convenience, a solution of hydroxylamine hydrochloride in hydrochloric acid was used. The requisite amounts of acid to give a 4*N* test solution and the hydroxylamine could then be added simultaneously. Two millilitres of a 2·5 per cent. w/v solution of hydroxylamine hydrochloride in 10*N* hydrochloric acid were added to separating funnels containing 2-ml aliquots of leach liquors. The acid was added cautiously to prevent loss of solution by the too rapid evolution of carbon dioxide and nitrous oxide. Heat was generated during the addition of the acid, and caused the temperature of the solution to exceed 30° C. In order to prevent the subsequent extraction of any tungsten present, the contents of the funnels were allowed to cool for a few minutes to a temperature of 20° to 25° C, then 0·6 ml of a 1 per cent. solution of dithiol in isoamyl acetate were added, and the funnels were shaken three or four times over a period of 15 minutes to facilitate the formation and extraction of the molybdenum complex. The molybdenum was extracted quantitatively, provided that a fresh solution of dithiol in the ester, prepared daily, was used.

#### PREPARATION OF STANDARDS—

A stock solution of molybdenum was prepared by dissolving 0·075 g of pure molybdenum trioxide in a few millilitres of *N* sodium hydroxide, then diluting with water and just acidifying with normal hydrochloric acid solution, and finally diluting to 500 ml. The stock solution containing 100 µg of molybdenum per ml was diluted with water to give two solutions, one containing 1 µg of molybdenum per ml (solution *A*) and the other 10 µg of molybdenum per ml (solution *B*). From these two solutions a series of standards, successive standards differing in their molybdenum content by about 30 per cent., were prepared. Then 0·1 to 2·0-ml aliquots of solution *A* and 0·3 to 1·0-ml aliquots of solution *B* were put by pipette into 16-mm × 150-mm test-tubes. Water was added to make up the volume to 2 ml, and 2 ml of 10*N* hydrochloric acid containing 2·5 per cent. w/v of hydroxylamine hydrochloride were added to each tube; 0·5 ml of a freshly prepared 1 per cent. solution of dithiol in isoamyl acetate was added, and the tubes were shaken four or five times over a period of 15 to 20 minutes to facilitate the formation and extraction of the molybdenum - dithiol complex. As the ester was not hydrolysed appreciably while in contact with the 5*N* hydrochloric acid, the standards were stable. Provided that the tubes were plugged with cotton-wool, to prevent loss of the ester by evaporation, the standards could be used for several days.

These standards covered the range 0·1 to 10·0 µg of molybdenum, corresponding to 1 to 100 p.p.m. in soils. The effective range of the method could be extended either by the use of additional standards containing up to 20 µg of molybdenum or, preferably, by taking only 1-ml aliquots of the leach liquors and only 1 ml of 10*N* hydrochloric acid containing hydroxylamine, and then forming and extracting the molybdenum - dithiol complex as described above.

**INTERFERENCES—**

Tungsten did not interfere, even when 100  $\mu\text{g}$  (equivalent to 1000 p.p.m. of tungsten in a soil) were present in the test solutions. No tungsten - dithiol complex was extracted into the ester under the conditions used for the extraction of the molybdenum - dithiol complex.

As in the tungsten determination, interference from iron and other elements forming insoluble hydroxides was avoided by the use of an aqueous leach of the melt from an alkaline fusion. With soils high in copper, some passed into the carbonate leach liquors, but the black insoluble copper - dithiol complex that formed, and collected at the interface between the ester and the aqueous phase, was removed on washing the ester with concentrated hydrochloric acid.

The use of hydroxylamine to prevent interference from nitrites and oxidation products of dithiol has been described above. No interference caused by the occlusion of molybdenum by the gelatinous silicic acid that formed when the carbonate leach liquors were acidified was encountered.

**METHOD FOR MOLYBDENUM****REAGENTS—**

*Flux*—A mixture of 5 parts by weight of sodium carbonate, 4 parts of sodium chloride and 1 part of potassium nitrate ground to pass through an 80-mesh sieve.

*Hydrochloric acid, sp.gr. 1.18.*

*Hydroxylamine hydrochloride*—Dissolve 2.5 g of the solid in 10 ml of water and then add 90 ml of concentrated hydrochloric acid.

*isoAmyl acetate*—Analytical-reagent grade.

*Toluene-3:4-dithiol*—Melt the contents of a 1-g ampoule at 30° to 40° C, and dissolve the reagent in 100 ml of *isoamyl acetate*.

*Standard molybdate solution*—Prepare a solution containing 100  $\mu\text{g}$  of molybdenum per ml by dissolving 0.075 g of pure molybdenum trioxide in a few millilitres of *N* sodium hydroxide, dilute with water, just acidify with *N* hydrochloric acid and dilute finally to 500 ml.

**PROCEDURE—**

Mix 0.25 g of soil (-80 mesh) with 1.25 g of flux in a 3-cm  $\times$  3-cm nickel crucible, and heat to obtain a quiet melt. Cool, add 3 ml of hot water, and preferably set aside overnight, or use a glass rod and heat gently to free the melt from the crucible. Transfer the contents of the crucible to a graduated test-tube, wash out the crucible with two small volumes of water, and then make up to the 5-ml mark on the tube. Heat the tube in a boiling-water bath for 10 minutes to ensure the complete break-up of the melt. Set the tube aside to cool, and to allow insoluble matter to settle out. Transfer a 2-ml aliquot of the supernatant liquor to a cylindrical separating funnel (diameter 16 mm), and add 2 ml of hydroxylamine hydrochloride solution cautiously. Allow the contents of the funnel to cool to 20° to 25° C. Add 0.6 ml of dithiol solution in *isoamyl acetate*, and then shake the funnel gently four or five times, over a period of 15 minutes, to facilitate the formation and extraction of the molybdenum complex. Drain off the lower aqueous phase, add 4 ml of concentrated hydrochloric acid and shake the funnel for 30 seconds to clarify the ester. Set aside for a few moments to allow the phases to separate. Compare, visually against a white background, the colour intensity of the yellow-green molybdenum - dithiol complex in the ester layer with standards prepared in 16-mm  $\times$  150-mm test-tubes.

**RESULTS**

The molybdenum contents of 5 soils and 4 shales were determined. The results for four replicate determinations by the field method are given in Table III, together with results obtained spectrographically.

**CONCLUSIONS**

The methods described allow the determination of tungsten over the range 4 to 400 p.p.m. and molybdenum over the range 1 to 100 p.p.m. in soils. By simple modifications of the procedures greater amounts of both metals can be determined. The results obtained indicate that the methods are sufficiently accurate for geochemical prospecting purposes. The methods are rapid, 30 or more determinations can be made per man per day; and, as only simple apparatus is required, the methods are suitable for use in the field.

TABLE III

## DETERMINATION OF MOLYBDENUM IN SOILS AND SHALES

Samples 1 to 5 are soils and 6 to 9 are shales

Sample No.	Molybdenum found by field method, p.p.m.				Mean, p.p.m.	Molybdenum found spectrographically, p.p.m.
	1	2	3	4		
1 (soil)	5,	8,	8,	7	7	5
2 (soil)	9,	10,	10,	10	10	10.5
3 (soil)	9,	18,	12,	13	13	15
4 (soil)	40,	32,	30,	28	32	30
5 (soil)	30,	25,	35,	25	29	30.5
6 (shale)	16,	20,	18,	18	18	18
7 (shale)	50,	60,	60,	60	58	40
8 (shale)	150,	160,	160,	160	158	135
9 (shale)	200,	200,	260,	200	215	165

I am indebted to Dr. J. S. Webb of the Royal School of Mines for supplying soils containing anomalous amounts of tungsten, and also to Dr. J. R. Butler and Mr. H. Le Riche of the Rothamsted Experimental Station for supplying samples and for permission to quote results obtained by them. This paper is published by permission of the Director of the Chemical Research Laboratory.

## REFERENCES

- Hunt, E. C., North, A. A., and Wells, R. A., *Analyst*, 1955, **80**, 172.
- Ward, F. N., U.S. Geological Survey Circular 119, 1951.
- , *Anal. Chem.*, 1951, **23**, 788.
- Hammen, J. H., *Analyst*, 1940, **65**, 152.
- Miller, C. C., and Lowe, A. J., *J. Chem. Soc.*, 1940, 1258.
- Miller, C. C., *Ibid.*, 1941, 792.
- , *Ibid.*, 1943, 72.
- , *Analyst*, 1944, **69**, 109.
- Piper, C. S., and Beckwith, R. S., *J. Soc. Chem. Ind.*, 1948, **67**, 374.
- Vaughan, E. J., and Whalley, C., *J. Iron & Steel Inst.*, 1947, **155**, 535.
- Wells, J. E., and Pemberton, R., *Analyst*, 1947, **72**, 185.
- Bagsshawe, B., and Truman, R. J., *Ibid.*, 1947, **72**, 189.
- Bickford, C. F., Jones, W. S., and Keene, J. S., *J. Amer. Pharm. Ass., Sci. Ed.*, 1948, **37**, 255.
- Short, H. G., *Analyst*, 1951, **76**, 710.
- Allen, S. H., and Hamilton, M. B., *Anal. Chim. Acta*, 1952, **7**, 483.
- Crouthamel, C. E., and Johnson, C. E., *Anal. Chem.*, 1954, **26**, 1284.

CHEMICAL RESEARCH LABORATORY  
TEDDINGTON, MIDDX.

April 25th, 1956

## Non-stationary Platinum Electrodes for the Amperometric Determination of Cysteine and Cystine

BY B. C. RAY SARKAR AND R. SIVARAMAN

A rotating platinum electrode and a vibrating one have been described for the amperometric determination of the sulphydryl group in cysteine from semi-micro and micro-quantities of the sample. The technique has also been applied to the determination of cystine after its conversion to cysteine.

SEVERAL authors<sup>1,2,3,4,5,6,7</sup> have made use of the amperometric technique developed by Kolthoff and Harris<sup>8</sup> for the determination of the sulphydryl group in biological materials. One of the essential requirements in this connection is the use of a non-stationary type of platinum electrode as an indicator electrode. In essence, this electrode is a platinum wire, which is made to rotate or vibrate in order to facilitate the titration. There has been some work on the development of suitable mechanical systems for such a purpose. Kolthoff and Harris<sup>8</sup> and lately Herbert and Denson<sup>9</sup> have described the devices employed for rotation

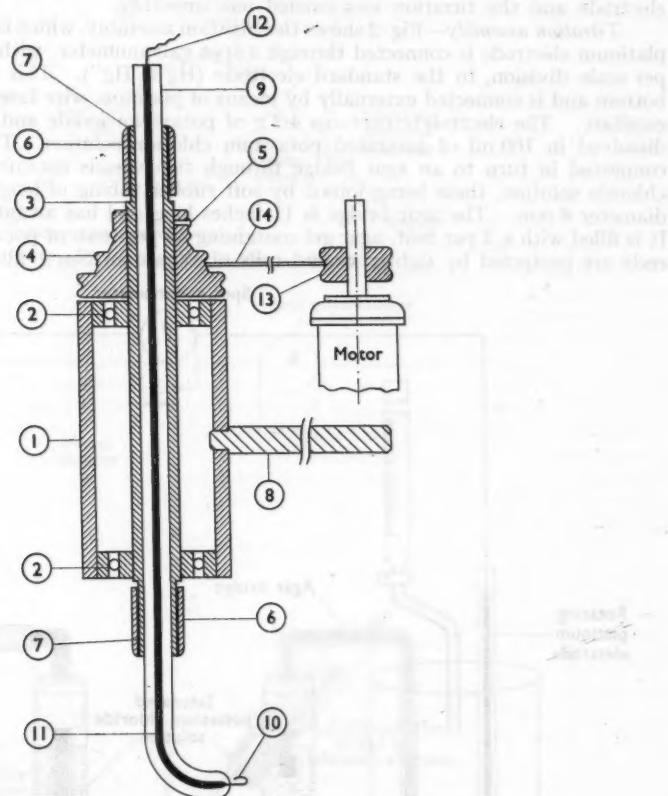
Nov., 1956]

## DETERMINATION OF CYSTEINE AND CYSTINE

669

of the electrode, and the details of several types of vibrating electrode used in amperometric and polarographic titrations have been given by other workers.<sup>10,11,12,13,14,15,16,17</sup> Studies of the behaviour of vibrating platinum micro-electrodes have been made, rather elaborately, by Lindsey<sup>13,14</sup> and Dirscherl and Otto<sup>16,17</sup>. The possibility of preparing similar electrodes from available materials in this laboratory has been explored. This paper gives a description of each of the two types developed, with the results obtained in the determination of cysteine. Incidentally, cystine was also determined amperometrically by reducing it to cysteine. The principle followed in the reduction was that outlined by Kolthoff and Lingane,<sup>18</sup> and utilised recently by Carter<sup>19</sup> in the amperometric determination of disulphides in intact proteins. In this reaction one mole of cysteine was derived from one mole of cystine.

For the purpose of comparison, cysteine was determined volumetrically by utilising the reaction of the sulphhydryl group with *o*-iodosbenzoic acid<sup>20</sup> and with potassium ferricyanide.<sup>21,22,23</sup>



- 1 = outer brass cylinder
- 2 = ball bearings
- 3 = inner brass tube
- 4 = cone pulley
- 5 = screw
- 6 = sockets
- 7 = ebonite sleeves
- 8 = handle

- 9 = capillary glass tube having an external diameter of 7.2 mm and an internal diameter of 1.5 mm
- 10 = platinum electrode with a diameter of 0.5 mm and a length of about 8.0 mm
- 11 = mercury in the capillary
- 12 = copper wire
- 13 = pulley of the motor
- 14 = belt

Fig. 1. Rotating platinum electrode showing constructional details

**APPARATUS—**

**Rotating platinum electrode**—Relevant constructional details of the system employed for the rotation of the platinum electrode are shown in Fig. 1. A glass capillary tubing having a platinum wire sealed to its lower end was filled with mercury up to a certain length. It was then fixed inside a piece of brass tubing with a pair of ebonite sleeves and metallic sockets. The brass tubing in turn was kept in position with a pair of ball bearings fixed inside the two ends of a thick-walled metallic jacket, which could be clamped to a stand by means of a handle. The electrode could be rotated with the help of a belt passing around the cone-pulley at the top of the brass tubing and the pulley of a motor of variable speed. For the present work the rotation was fixed at about 130 r.p.m. One end of a copper wire was connected to the galvanometer and the other end was dipped in the mercury inside the glass tubing. Electrical contact of the system was maintained perfectly during rotation of the electrode and the titration was carried out smoothly.

**Titration assembly**—Fig. 2 shows the titration assembly, which is as follows. The rotating platinum electrode is connected through a spot galvanometer, with a sensitivity of  $0.007 \mu\text{A}$  per scale division, to the standard electrode ( $\text{Hg} \rightleftharpoons \text{Hg}''$ ). This contains mercury at the bottom and is connected externally by means of platinum wire fused to the lower end of the capillary. The electrolyte contains 4.2 g of potassium iodide and 1.3 g of mercuric iodide dissolved in 100 ml of saturated potassium chloride solution. The standard electrode is connected in turn to an agar bridge through two vessels containing saturated potassium chloride solution, these being joined by soft rubber tubing of length 2 feet and of internal diameter 6 mm. The agar bridge is 11 inches long and has an internal diameter of 5 mm. It is filled with a 3 per cent. agar gel containing 30 per cent. of potassium chloride, and both ends are protected by tightly wound rolls of Whatman No. 1 filter-paper.

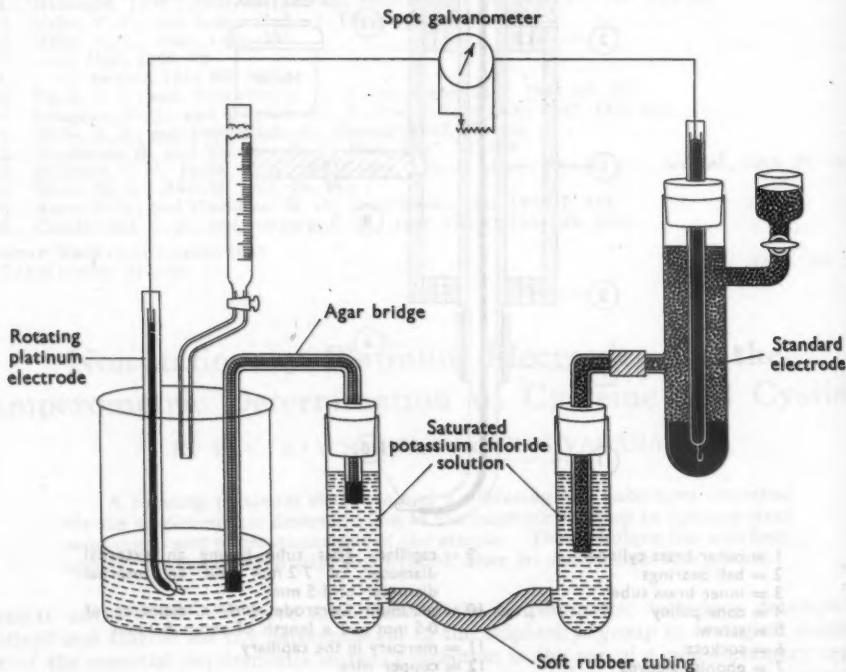


Fig. 2. Titration assembly

**Vibrating platinum electrode**—This has been devised especially for dealing with a much smaller sample. Details are shown in Fig. 3. The system was made essentially from an

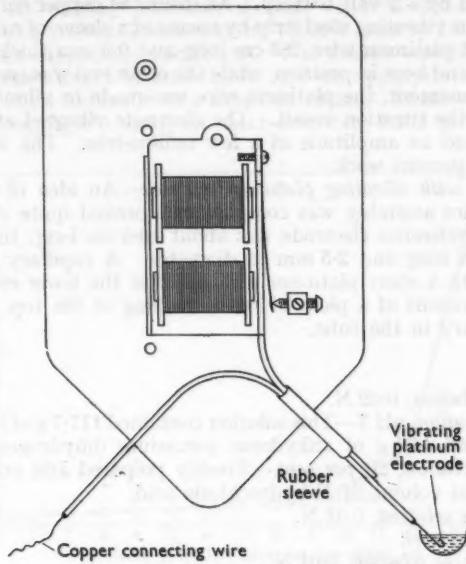
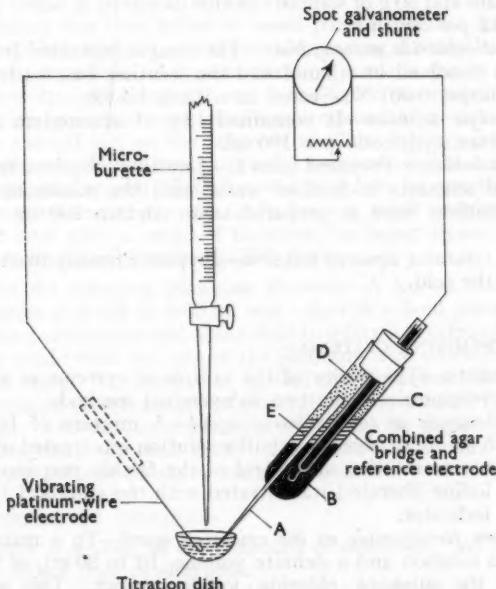


Fig. 3. Vibrating platinum electrode



A = potassium chloride - agar bridge  
 B = mercury for the reference electrode  
 C = platinum electrode  
 D = saturated potassium chloride solution  
 E = reference electrolyte solution

Fig. 4. Titration assembly with vibrating platinum electrode

electric buzzer operated by a 2-volt battery. An insulated copper connecting wire was fixed to the bottom part of the vibrating steel strip by means of a sleeve of rubber tubing. Through one end of this a small platinum wire, 2·5 cm long and 0·5 mm thick, having a loop at the free end was pushed in and kept in position, while the other end was connected to the galvanometer. By proper adjustment, the platinum wire was made to vibrate freely inside a small porcelain dish used as the titration vessel. The electrode vibrated at a frequency of about 60 cycles per second and an amplitude of a few millimetres. The vibration was found to be satisfactory for the present work.

*Titration assembly with vibrating platinum electrode*—An idea of this may be obtained from Fig. 4. The entire assembly was compact and proved quite convenient. The combined agar bridge and reference electrode was about 10·5 cm long; the potassium chloride-agar bridge was 7·5 cm long and 2·5 mm in diameter. A capillary tube 5·5 cm long and 2·5 mm in diameter with a short platinum wire fused at the lower end was kept inside the reference electrode by means of a piece of rubber tubing at the top. External connection was through the mercury in the tube.

#### REAGENTS—

*o-Iodosobenzoate solution, 0·02 N.*

*Phosphate buffer solution, pH 7*—This solution contained 117·7 g of anhydrous dipotassium hydrogen phosphate and 44·1 g of anhydrous potassium dihydrogen phosphate per litre.

*Potassium iodide solution, 20 per cent.*—Freshly prepared and acidified just before use by mixing with an equal volume of *N* hydrochloric acid.

*Sodium thiosulphate solution, 0·01 N.*

*Starch solution, 1 per cent.*

*Potassium ferricyanide solution, 0·01 N.*

*Sulphate - chloride - iodide solution*—This contained 5 g of potassium iodide, 10 g of anhydrous zinc sulphate and 50 g of sodium chloride dissolved in water and diluted to 200 ml.

*Sulphuric acid, 12 per cent. v/v.*

*1(+)-Cysteine hydrochloride monohydrate*—The sample (obtained from Merck & Co. Inc.) weighing 1·755 g was dissolved in ethanol and the solution was made up to 1 litre.

*Silver nitrate solution, 0·001 N*—Stored in a dark bottle.

*Supporting electrolyte solution*—It contained 12 g of ammonium nitrate and 50 ml of concentrated ammonium hydroxide per 100 ml.

*Standard cystine solutions*—Prepared from 1(+)cystine (obtained from Merck & Co. Inc.) by dissolving weighed amounts in distilled water with the minimum quantities of hydrochloric acid. The solutions were so prepared as to contain 200 mg, 240 mg, 300 mg and 400 mg per 100 ml.

*Sodium sulphite, saturated aqueous solution*—Prepared freshly from a high-grade sample each day and kept in the cold.

*Ethanol, absolute.*

#### PROCEDURE FOR DETERMINING CYSTEINE—

(a) *VOLUMETRIC METHODS*—The purity of the sample of cysteine or its concentration in a solution was checked volumetrically by two independent methods.

(i) *With o-iodosobenzoate as the oxidising agent*—A mixture of 10 ml of the *o*-iodosobenzoate solution and 5 ml of the phosphate buffer solution was treated with a definite volume, 10 to 30 ml, of the cysteine solution and 20 ml of the freshly prepared acidified potassium iodide solution. The iodine liberated was titrated with the standard thiosulphate solution, starch being used as indicator.

(ii) *With potassium ferricyanide as the oxidising agent*—To a mixture of 20 ml of the potassium ferricyanide solution and a definite volume, 10 to 30 ml, of the cysteine solution were added 20 ml of the sulphate - chloride - iodide reagent. This was acidified by the addition of 12 ml of the sulphuric acid. The iodine liberated was titrated as usual. If only an acidified iodide solution is used in place of the sulphate - chloride - iodide reagent, the end-point would be difficult to detect because of the reversible nature of the reaction.

(b) *AMPEROMETRIC TITRATION*—The rotating platinum electrode was used for dealing with 1 ml or more of the test solution, and the vibrating electrode for titrating much smaller volumes, as has already been mentioned.

(i) *Titration with the rotating platinum electrode*—Into a 250-ml Pyrex-glass beaker containing 29 ml of absolute ethanol were put by pipette exactly 1 to 2 ml of the cysteine solution and 1 ml of the supporting electrolyte. The beaker was then placed in position. After the necessary connections had been made and an appropriate shunt put across the galvanometer, the platinum electrode was made to rotate. There was an initial diffusion current, which became negligibly small on short-circuiting for 2 to 4 minutes.

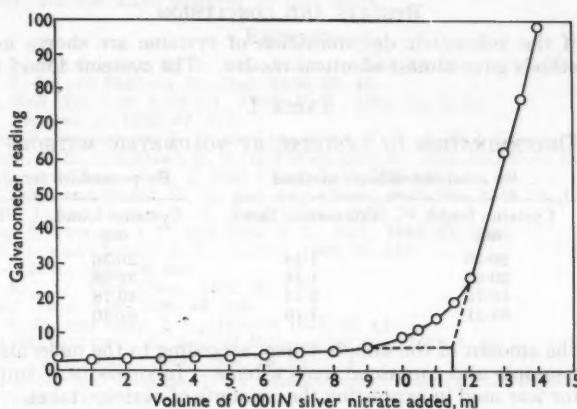


Fig. 5. Typical titration curve

Silver nitrate solution was then added in small portions from a burette protected from light by being wrapped in black paper, and the steady reading of the galvanometer corresponding to each addition was recorded. A typical titration curve is shown in Fig. 5. The point of intersection of the two straight lines as shown in the figure was projected on to the abscissa, and the corresponding end-point in terms of silver nitrate solution consumed was determined. Blank titrations were carried out on the reagents to allow for any correction in the determination of the volume of silver nitrate actually required in the reaction with cysteine. With the reagents used, the correction factor was found to be practically nil. There was no indication of poor response of the electrode from a small number of titrations. The electrode was cleaned only after a series of titrations by being dipped for a few minutes in 2 N nitric acid and washed finally with distilled water.

(ii) *Titration with the vibrating platinum electrode*—A known volume of the cysteine solution within the range of 0.025 to 0.05 ml was taken in a 5-ml porcelain dish. An equal volume of the supporting electrolyte and about 0.25 to 0.50 ml of ethanol were added. Necessary connections were made with the loop of the platinum wire vibrating beneath the surface of the solution in the dish. Titration was carried out as before, this time a micrometer syringe fitted with a straight glass capillary jet preferably being used for the delivery of standard silver nitrate solution. The curves obtained were similar in nature to those found when the rotating platinum electrode was used. Blank titrations were also carried out for determining the correct volume of silver nitrate required.

#### PROCEDURE FOR DETERMINING CYSTINE—

The sample as such was used as the standard of reference. As before, titrations were carried out by using either type of electrode.

(i) *Titration with the rotating platinum electrode*—To 29 ml of absolute ethanol in a 250-ml Pyrex-glass beaker were added 1 ml of the cystine solution of known concentration, 1 ml of the supporting electrolyte and 2 ml of the sodium sulphite solution. The electrode was so adjusted that the platinum wire could rotate just above the precipitate of sodium sulphite formed. Titration with silver nitrate was carried out as before. The experiment was repeated with the other cystine solutions of various concentrations. Blank titrations were also carried out.

(ii) *Titration with the vibrating platinum electrode*—To 0.5 ml of ethanol in a 5-ml porcelain dish were added a small fraction of 1 ml of cystine solution of a known concentration, 0.1 ml of the supporting electrolyte and 0.2 ml of the sodium sulphite solution. The platinum wire was then made to vibrate above the precipitate of sodium sulphite formed at the bottom. Titration was subsequently carried out as described above. As usual, titrations were also carried out to determine the blank value.

### RESULTS AND CONCLUSION

The results of the volumetric determination of cysteine are shown in Table I. Both the volumetric methods gave almost identical results. The cysteine found was about 16 per

TABLE I  
DETERMINATION OF CYSTEINE BY VOLUMETRIC METHODS

Cysteine taken, mg	By o-iodosobenzoate method		By potassium ferricyanide method	
	Cysteine found, mg	Conversion factor	Cysteine found, mg	Conversion factor
17.55	20.36	1.16	20.36	1.16
26.33	30.67	1.16	30.68	1.17
35.10	40.75	1.16	40.78	1.16
52.65	61.11	1.16	61.40	1.17

cent. higher than the amount of the sample taken, according to the molecular formula. This indicated that the sample also contained free cysteine. In subsequent amperometric determination, this factor was used in expressing the amounts of cysteine taken. Relevant results

TABLE II  
AMPEROMETRIC DETERMINATION OF CYSTEINE

Test solution, ml	Cysteine present, mg	With rotating platinum electrode			With vibrating platinum electrode		
		Cysteine found, mg	Difference, %	Test solution ml	Cysteine present, mg	Cysteine found, mg	Difference, %
1.0	2.036	2.03	-0.30	0.025	0.0509	0.052	+2.16
1.5	3.065	3.05	-0.49	0.040	0.0814	0.081	-0.49
2.0	4.075	4.06	-0.37	0.050	0.1018	0.101	-0.79

for the amperometric determination are presented in Table II. While various amounts of cysteine were determined, by means of the rotating as well as the vibrating electrode, the percentage recovery was found to be on the whole quite high. Although it has been the practice to keep the volume of test solutions constant in such titrations, the results were not found to be affected when the volumes varied within the range used in the present work.

TABLE III  
AMPEROMETRIC DETERMINATION OF CYSTINE

Test solution, ml	Cystine present, mg	With rotating platinum electrode			With vibrating platinum electrode		
		Cystine found, mg	Difference, %	Test solution ml	Cystine present, mg	Cystine found, mg	Difference, %
1.0	2.00	1.97	-1.50	0.0250	0.050	0.0516	3.20
1.0	2.40	2.36	-1.67	0.0375	0.075	0.0768	2.40
1.0	3.00	2.98	-0.67	0.0500	0.100	0.1020	2.00
1.0	4.00	3.98	-0.50	0.0625	0.125	0.1272	1.76

The results of determining different amounts of cystine after its conversion to cysteine are shown in Table III. The percentage recovery on the whole was slightly less than that observed for cysteine. However, the tendency for the percentage recovery to be greater with higher amounts of cystine was also noted here. These results and the convenience

of carrying out the titrations suggest the value of the electrodes used. Although volumetric methods proved to be quite simple, the amperometric technique might be preferred for dealing with biological samples. This study was merely a standardisation of the method involving use of the rotating and vibrating electrodes with a view to their application in work requiring the determination of sulphhydryl groups in biological materials.

We express our thanks to Dr. D. S. Kothari, Scientific Adviser, Ministry of Defence, New Delhi, India, for his kind interest in this work.

#### REFERENCES

1. Benesch, R., and Benesch, R. E., *Arch. Biochem.*, 1948, **19**, 35.
2. Benesch, R. E., and Benesch, R., *Ibid.*, 1950, **28**, 43.
3. Hata, T., *Bull. Res. Inst. Food Sci., Kyoto Univ.*, 1951, No. 4, 45.
4. Cecil, R., *Biochem. J.*, 1950, **47**, 572.
5. Wiessman, N., Schoenbach, E. B., and Armistead, E. B., *J. Biol. Chem.*, 1950, **187**, 153.
6. Schoenbach, E. B., Armistead, E. B., and Wiessman, N., *Proc. Soc. Expt. Biol. Med.*, 1950, **44**, 73.
7. Ling, C. T., and Chow, B. F., *J. Biol. Chem.*, 1953, **202**, 445.
8. Kolthoff, I. M., and Harris, W. E., *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 161.
9. Herbert, F. J., and Denson, J. R., *Anal. Chem.*, 1954, **26**, 440.
10. Rosenberg, S., Perrone, J. C., and Kirk, P. L., *Ibid.*, 1950, **22**, 1186.
11. Harris, E. D., and Lindsey, A. J., *Analyst*, 1951, **76**, 647.
12. ———, *Ibid.*, 1951, **76**, 650.
13. Lindsey, A. J., *J. Phys. Chem.*, 1952, **56**, 439.
14. ———, *Anal. Chim. Acta*, 1955, **13**, 200.
15. Roberts, E. R., and Meek, J. S., *Analyst*, 1952, **77**, 43.
16. Dirscherl, W., and Otto, K., *Leybold Polarograph. Ber.*, 1953, **1**, 49.
17. ———, *Chemie-Ing. Techn.*, 1954, **26**, 321.
18. Kolthoff, I. M., and Lingane, J. J., "Polarography," Interscience Publishers Inc., New York, 1952, Volume II, p. 944.
19. Carter, J. R., *Science*, 1954, **120**, 895.
20. Hellerman, L., Chinard, F. P., and Ramsdell, P. A., *J. Amer. Chem. Soc.*, 1941, **63**, 2551.
21. Mason, H. L., *J. Biol. Chem.*, 1930, **86**, 623.
22. Anson, M. L., *J. Gen. Physiol.*, 1942, **25**, 355.
23. Mirsky, A. E., *Ibid.*, 1941, **24**, 725.

DEFENCE SCIENCE ORGANISATION  
MINISTRY OF DEFENCE  
GOVERNMENT OF INDIA  
NEW DELHI

March 1st, 1956

## Ministry of Agriculture, Fisheries and Food

### FOOD STANDARDS COMMITTEE

#### REPORT ON EMULSIFYING AND STABILISING AGENTS

The Minister of Agriculture, Fisheries and Food, the Minister of Health and the Secretary of State for Scotland have approved for publication a Report of the Food Standards Committee's Preservatives Subcommittee making recommendations about the use of emulsifying and stabilising agents in foods.

Before deciding what action should be taken on these recommendations, the Ministers concerned will consider any representations from interested parties. They should be sent to the Assistant Secretary, Food Standards and Hygiene Division, Ministry of Agriculture, Fisheries and Food, Great Westminster House, Horseferry Road, London, S.W.1, to arrive not later than November 30th, 1956.

Copies of the Report may be obtained from H.M. Stationery Office, price 9d. (plus postage).

## British Standards Institution

### NEW SPECIFICATION\*

B.S. 894: 1956. Ubbelohde Apparatus for Flow and Drop Points. Price 3s. 6d.

### AMENDMENT SLIP\*

A PRINTED slip bearing amendments to a British Standard has been issued by the Institution, as follows—

PD 2571—Amendment No. 1 (September, 1956) to B.S. 718:1953. Density Hydrometers and Specific Gravity Hydrometers.

\* Obtainable from the British Standards Institution, Sales Department, 2 Park Street, London, W.1.

## Book Review

**ORGANIC ANALYSIS. Volume II.** Edited by J. MITCHELL, jun., I. M. KOLTHOFF, E. S. PROSKAUER and A. WEISSBERGER. Pp. viii + 372. New York and London: Interscience Publishers Inc. 1954. Price \$8.50; 68s.

This book contains nine review articles on various aspects of organic analysis; it is not the second volume of a general textbook on the subject, as the title might suggest. Broadly, the subject matter is divided equally between chemical methods on the one hand and physical and instrumental methods on the other; there is, of course, some overlap.

The longest article, perhaps the most generally interesting, is that on the determination of esters; it is well worth study by those who consider that there is no more to it than heating with ethanolic alkali, and it might have given a clue to the author of a paper published some years ago as to why the *p*-nitrobenzoates of propan-2-ol and pentan-1-ol were reported (erroneously) as melting at about 55° C. The article on the determination of nitro, nitroso and nitrate groups follows a straightforward course, but that on the micro-determination of carboxyl groups seems out of step with the lengthy bibliography.

It hardly seems that aluminium lithium hydride has only been with us since 1947; its analytical applications are set out and some suggestions made for their future extension.

Recent issues of *Analytical Abstracts* reveal an increasing interest in coulometric methods. The technique is described, but the peculiar feature here is that there is very little pertaining to its use in organic analysis. Polarography may be speedy, but is full of pitfalls; recent work has indicated the cause of some errors and difficulties, and these, as well as the advantages of the technique, are discussed.

Methods based on reaction rate are not generally popular, but they do find useful application for substances that exert a catalytic effect on a reaction and in the analysis of some mixtures. One of the best known examples of phase-solubility analysis is the evaluation of commercial DDT; usually, however, such methods are lengthy.

This volume concludes with a survey of counter-current distribution, another relatively recent addition to the analyst's armoury, particularly useful in the separation of substances of unknown chemical properties, such as biologically active bodies.

There is certainly a niche in the library for the books in this series, for there is nothing quite like them; the nearest approach are the review numbers of *Analytical Chemistry*, but these usually survey the work of the preceding year or so rather than deal with a subject as an entity.

B. A. ELLIS

## Publications Received

- SYSTEMATIC SEMI-MICRO QUALITATIVE ANALYSIS TABLES FOR INORGANIC SUBSTANCES.** Part I, Part II and Combined. By E. MINSHALL, M.Sc., F.R.I.C. Pp. 50; 48; 94. London: Macdonald & Evans Ltd. 1956. Price: Part I, 5s.; Part II, 5s.; Combined, 8s. 6d.  
*Intended for students from G.C.E. (Advanced) to A.R.I.C. level.*
- ORGANO-METALLIC COMPOUNDS.** By G. E. COATES, M.A., D.Sc., F.R.I.C. Pp. viii + 197. London: Methuen & Co. Ltd.; New York: John Wiley & Sons Inc. 1956. Price 12s. 6d.
- INORGANIC QUALITATIVE ANALYSIS: SEMI-MICRO METHODS.** By H. HOLNESS, M.Sc., F.R.I.C. Second Edition. Pp. viii + 152. London: Sir Isaac Pitman & Sons Ltd. 1956. Price 12s. 6d.
- TRAITÉ DE MICRO-ANALYSE MINÉRALE: QUALITATIVE ET QUANTITATIVE.** Volume III. By C. DUVAL. Pp. 548. Paris: Presses Scientifiques Internationales. 1956.
- SUPPLEMENT TO MELLOR'S COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY.** Supplement II. Part 1—F, Cl, Br, I, At. Editorial Board: H. V. A. BRISCOE, D.Sc., A.R.C.S., D.I.C., F.R.I.C., A. A. ELDREDGE, B.Sc., F.R.I.C., and G. M. DYSON, M.A., D.Sc., F.R.I.C., M.I.Chem.E., F.Inst.Pet. Pp. lii + 1153. London, New York and Toronto: Longmans, Green & Co. Ltd. 1956. Price 170s.
- QUANTITATIVE INORGANIC ANALYSIS: A STUDENT'S HANDBOOK.** By J. REILLY, M.A., Sc.D., F.R.I.C., F.Inst.P., and D. G. O'DONOVAN, M.Sc., Ph.D. Pp. 126. Cork: Cork University Press. 1956. Price 7s. 6d., limp bound; 10s. 6d., stiff bound.

os-  
nce  
the  
ect  
tru-  
a of  
with  
ears  
sly)  
ups  
ems  
ical  
ods.  
g to  
has  
the  
ation  
res.  
DT;  
vely  
s of  
uite  
ally  
is  
t I,  
ion:  
197.  
6d.  
I.C.  
Price  
By  
ICAL  
. A.  
. M.  
New  
D.,  
sity